ARGONNE NATIONAL LABORATORY

Laboratory Directed Research and Development

FY 1992 PROGRAM ACTIVITIES

ANNUAL REPORT

Strategic Planning Group
Office of the Director
December 10, 1992

DISCLAIMER

Argonne National Laboratory
Laboratory Directed Research and Development
1992 Annual Report

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INTRODUCTION

Program Overview

The purposes of Argonne's Laboratory Directed Research and Development (LDRD) Program are to encourage the development of novel concepts, enhance the Laboratory's R&D capabilities, and further the development of its strategic initiatives. Projects are selected from proposals for creative and innovative R&D studies which are not yet eligible for timely support through normal programmatic channels. Among the aims of the projects supported by the Program are establishment of engineering "proof-of-principle;" assessment of design feasibility for prospective facilities; development of an instrumental prototype, method, or system; or discovery in fundamental science.

Several of these projects are closely associated with major strategic thrusts of the Laboratory as described in Argonne's Five Year Institutional Plan, although the scientific implications of the achieved results extend well beyond Laboratory plans and objectives. The projects supported by the Program are distributed across the major programmatic areas at Argonne as indicated in the Laboratory's LDRD Plan for FY 1992. The following table displays the area of principal emphasis (indicated by an "X") as well as additional area(s) (indicated by an "O") to which a contribution was made by each FY 1992 project.

A brief description of Argonne's LDRD management process and a table of funding profiles for each project active in FY 1992 then follow. The FY 1992 DOE approved funding cap was $12 million or about 3% of Argonne's FY 1992 operating budget. Actual expenditures amounted to $8.86 million. Individual reports summarizing the purpose, approach, results and accomplishments of projects funded under Argonne's LDRD Program for FY 1992 comprise the bulk of this report.

Finally, Appendix A summarizes funding and topics of new projects begun to date in FY 1993.

1992 AREAS OF TECHNICAL IMPACT

Proposal Number	Advanced Accelerator and Detector Technology	X-Ray Techniques for Research in the Biological and Physical Sciences	Advanced Reactor Technology	Materials Science and Technology	Compu-tational Science and Technology	Biological Sciences	Environ-mental Science	Environ-mental Control and Waste Manage-ment Technology	Novel Concepts in Other Areas
92-006	X								
92-021	X								
92-022	X								
92-024	X								
92-031	X								
92-044	X								
91-025R1	X								
92-162	X	O							
90-001R2(a)	X	O							
92-166	X			O					
90-015R2	O	X							
91-002R1		X							
92-003	O	X							
90-001R2 (b)	O	X							
92-110	O	X							
90-001R2(c)	O	X							
91-022R1			X						
92-041			X						
92-047			X		O				
92-048			X						
92-052			X	O	O	O			
91-105R1			X					O	
92-177			X						
92-004	O	O		X					
92-023				X					
92-045				X					O
91-016R1				X					
91-039R1				X					
92-179				X					

Proposal Number	Advanced Accelerator and Detector Technology	X-Ray Techniques for Research in the Biological and Physical Sciences	Advanced Reactor Technology	Materials Science and Technology	Compu-tational Science and Technology	Biological Sciences	Environ-mental Science	Environ-mental Control and Waste Manage-ment Technology	Novel Concepts in Other Areas
92-008		O		X					
92-012					X		O		
91-038R1				O	X				
91-037R1					X		O		
91-036R1					X	O			
92-016			O		X				
92-109		O			X	O			
91-012R1						X			
92-108						X			
92-113						X			
92-160						X	O	O	
92-167						X			
92-169					O	X			
92-173						X			
92-180						X			
92-043			O			O	X	O	
91-010R1					O		X		
92-172					O		X		
92-181					O		X		
92-042			O					X	
92-049			O					X	
92-053			O	O				X	
92-168		O					O	X	
92-171								X	
92-175								X	
92-011				O					X
92-046			O	O					X
92-165	O								X
90-007R2									X

LDRD Management Process

Research and development activities at Argonne are organized under four associate laboratory directors who oversee the research conducted in 23 programmatic divisions. At the top of the organization is the laboratory director. He is assisted by the chief operations officer (who manages the Laboratory's physical plant and support functions), the chief financial officer, and the deputy to the laboratory director (who heads the Strategic Planning Office). This group of eight sit as the Strategic Planning Board and make final recommendations concerning laboratory directed R&D.

Responsibility for all final decisions concerning Argonne's LDRD program resides with the laboratory director. Certain responsibilities regarding funding, oversight, proposal evaluation, and project direction are delegated. The laboratory director also delegates selection of a fraction of LDRD projects to individual associate laboratory directors and holds back a small fraction for his own selections as well. The remainder of projects are selected by the Strategic Planning Board, which is also charged with recommending the proportion to be delegated. In FY 1992 the Board retained selection prerogative for projects totaling 85% of the LDRD budget. In FY 1993 the corresponding figure is 91%. The laboratory director coordinates the plans of the associate laboratory directors with plans for this larger centralized (FIGURE 1) portion. The delegated or decentralized (FIGURE 2) selections are reviewed, as are all proposals, by the Strategic Planning Office for adherence to DOE guidelines and laboratory administrative procedures. They are then reported to the laboratory director, who must approve them in terms of content and aggregate budget. At the end of the fiscal year, accomplishments of all LDRD projects are reported to the laboratory director and DOE. As examples, the 1993 calls for proposals and proposal guidance are attached as exhibits A, B, C and D.

Coordination, oversight, and administration of the centralized part of the Laboratory's LDRD program is the responsibility of the deputy to the laboratory director. He is assisted by the associate director of the Strategic Planning Group, who has direct responsibility for the day-to-day administration of the LDRD program and for coordination of LDRD reports and plans. Responsibility for the actual conduct of all laboratory directed R&D resides individually with the associate laboratory directors and their line managers.

The LDRD program is funded lab-wide through the Laboratory's indirect budget which derives from a uniform levy against all program operating budgets. The bulk of the initially planned LDRD budget is committed near the beginning of the fiscal year after most proposals have been evaluated (during September and early October). The laboratory director and the Strategic Planning Board maintain the option to fund new starts during the year either by increasing the total LDRD budget plan (within the DOE approved cap) or by redirection of previously authorized funds. Although many projects propose two or three year durations, funding levels and project selection are determined annually, based on technical progress and the Laboratory's strategic goals and resources.

Figure 1
Argonne's Centralized LDRD Program: Administrative Process

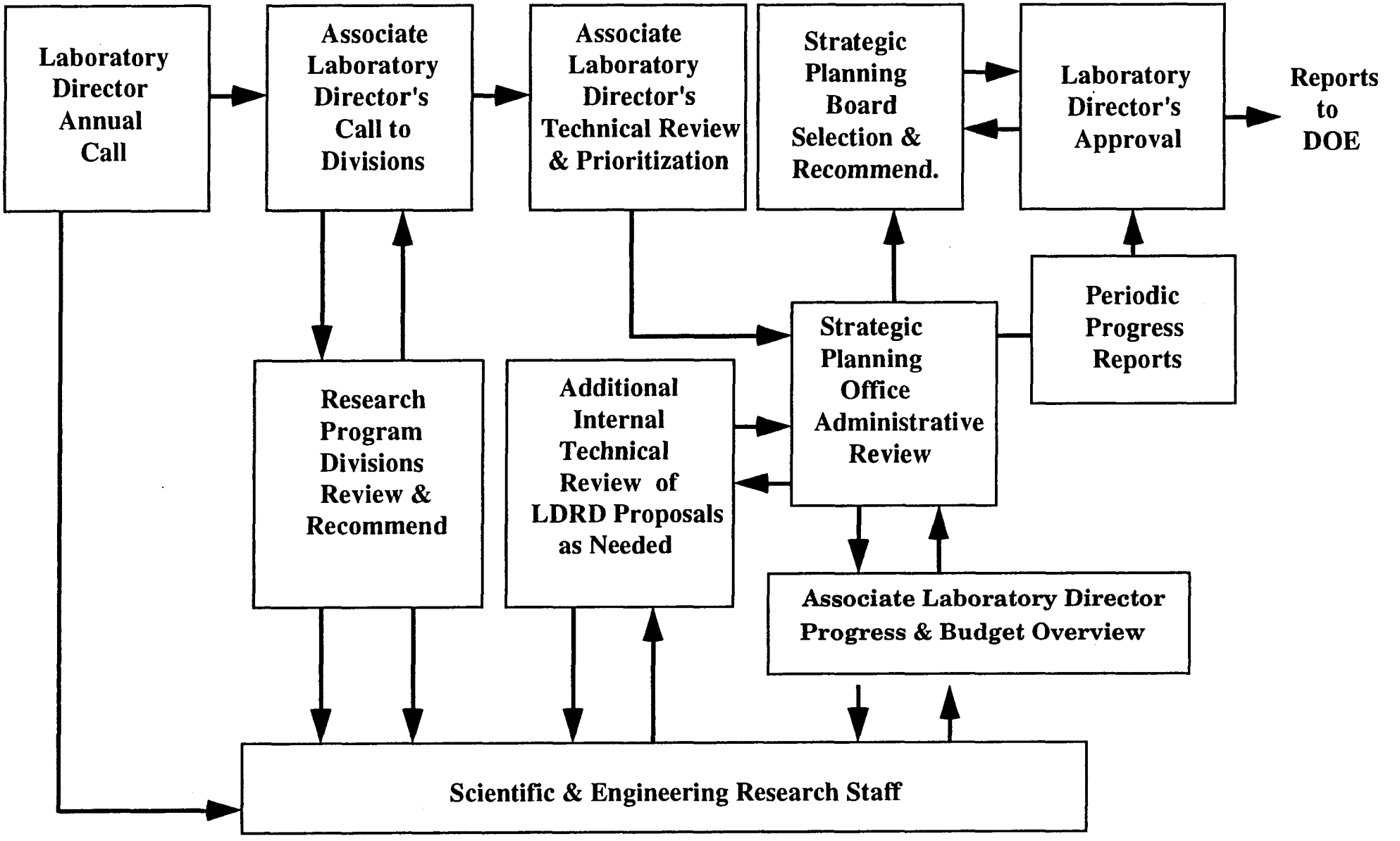

Figure 2
Argonne's Decentralized LDRD Program: Administrative Process

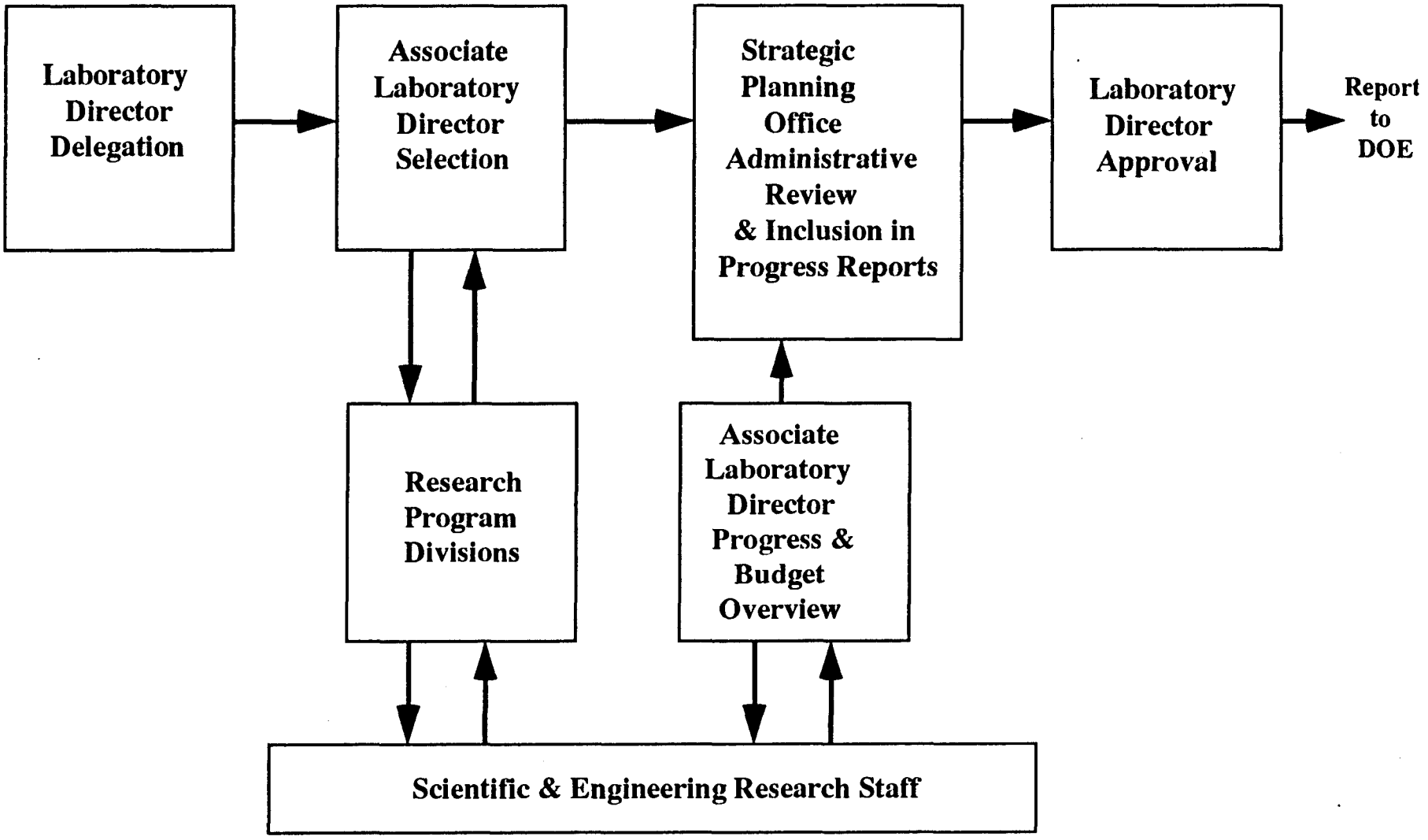

EXHIBIT A

Argonne National Laboratory

Intra-Laboratory Memo

July 1, 1992

TO: Argonne Technical Staff

FROM: A. Schriesheim

SUBJ: **FY 1993 LDRD Proposals**

We are again at the point in the fiscal year when proposals to the Laboratory Directed Research and Development (LDRD) Program are being solicited. I encourage you to consider what novel and innovative ideas in your field of expertise might qualify for LDRD support. This program is small compared to our major Laboratory programs, but it is most important for our future. It provides the nucleus for new programs and enhanced research capabilities for Argonne while testing exciting new concepts. Our vitality as a leading R&D resource for the nation is maintained and enhanced through the LDRD Program.

Current guidelines for LDRD proposals are being distributed to Associate Laboratory Directors. They will be available from division offices through which proposals should be submitted. I expect, as in previous years, we will assemble an impressive set of creative proposals.

AS:EK/mks

cc: J. Asbury
H. Drucker
F. Fradin
D. Moncton
C. Till

EXHIBIT B

Argonne National Laboratory

Intra-Laboratory Memo

July 1, 1992

TO: H. Drucker
F. Fradin
D. Moncton
C. Till

FROM: A. Schriesheim

SUBJ: **Call for FY 1993 Laboratory Directed Research and Development Proposals**

Guidelines for the submission of project proposals for consideration for support under the Laboratory Directed Research and Development Program are attached. Please transmit this call for proposals to staff in your area. With your programmatic divisions and staff, you should assure that each proposal received is technically reviewed and is screened for conformance with DOE and laboratory guidelines and acceptance criteria. Proposals which do not meet LDRD criteria will be returned.

We have now had over one-year's experience working under DOE 5000.4, the relevant order defining LDRD procedures and content, and have instituted some new procedures as a result. We will be asking for your office's help in implementing a few new tracking mechanisms to insure continued compliance.

A sample proposal format is attached and should be followed when developing proposals. In addition, a one-page evaluation form must be completed for each proposal.

We estimate that the FY 1993 funding level for the LDRD Program will total $10 million, unless future budget developments suggest a change at a later date. All proposals submitted to you, a memo stating your recommended priorities, and a list of technical staff who aided in the technical review process, should be submitted to Elton Kaufmann, Strategic Planning Office, no later than August 1, 1992. I plan to complete the review and allocation process with the Strategic Planning Board during October. Once our FY 1993 laboratory budget is better defined, I will notify you of the amounts set aside for our decentralized (ALD discretionary) LDRD program.

AS:EK/mks
Attachments
cc: J. Asbury
J. Day
M. Hennebry
R. Huebner
E. Kaufmann
J. O'Kelley
R. Teunis
E. VanBerkum
D. Weber

(7/1/92)

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT FUND

GUIDELINES AND PROCEDURES

PURPOSE

The ANL Laboratory Directed Research and Development Fund (LDRD) is established to support and encourage new ideas and novel approaches to scientific and technical problems. It is expected that efforts supported by the LDRD program will lead to new funded programs and new directions for the Laboratory, while taking maximum advantage of the talents and creativity of Argonne staff.

PROCEDURES

1. LDRD projects to be funded will be selected on a competitive basis from all proposals submitted by Argonne staff.

2. Each proposal will identify the principal investigator(s), state the purpose of the project, define the project's scope, and provide a brief summary of the planned project. The proposal should specify the amount of funding required and, if the project is expected to extend over more than one year, the funding needed until completion. Projects may not be extended beyond three years unless exceptional circumstances obtain.

3. A new proposal must explicitly state that no prior LDRD funding was devoted to any aspect of the work. If part or all of the project received prior-year LDRD funding, proposals must specify amounts by fiscal year and trace any changes in project title which have occurred. Any initiation or termination of subtasks within a project during or between fiscal years must be reported and explained.

4. The Strategic Planning Board will review the proposals submitted, obtain any additional information considered necessary, and submit its recommendations for funding to the Laboratory Director.

5. Budgets will be established for each of the approved projects, and appropriate accounts will be opened to collect charges.

6. Proposals may be submitted to the Strategic Planning Board at any time. However, a majority of the funds will be committed at the beginning of the fiscal year. A limited amount (up to 20%) may be reserved to allow the laboratory to support new projects or to respond to opportunities. In addition, funding allocations may be changed during the year by the Strategic Planning Board in response to new needs or opportunities.

7. The resources to be made available for the LDRD program will be established by the Laboratory Director, within the DOE approved maximum, prior to the beginning of the fiscal year.

8. A written report will be prepared by the principal investigator(s) for each year of each funded project. The report should summarize the technical results obtained by the study in sufficient detail and at a level of presentation so that a non-specialist can appreciate the content and accomplishments. The report should also identify opportunities for new funding resulting from the study. The report should be submitted within one month after the completion of the project or within one month after the end of the fiscal year, whichever comes first. Explicit guidelines on content and format of the report will be distributed before fiscal-year end.

PROGRAM SELECTION GUIDELINES

1. The LDRD program will be administered according to the guidelines established by DOE for the use of LDRD Funds (See Attachment A: Guidelines excerpted from DOE Order 5000.4, 2/28/91).

2. LDRD projects should emphasize scientific and technical excellence and be at the forefront of science and technology.

3. LDRD projects should offer the promise to enhance the Laboratory's capabilities and be relevant to the long-term Strategic View of the Laboratory. (See Section III of the FY 1992 - FY 1997 Institutional Plan.)

4. LDRD projects should involve adequate effort and resources to insure proposed ideas are thoroughly tested. However, LDRD projects will generally not exceed 1.5 FTE of effort plus M&S (total $200K in any one year and, if a multi-year project, should not exceed $500K in total). Separately identifiable tasks that can stand alone as LDRD projects should not be combined into larger, single PI, projects.

5. LDRD projects may not be used to substitute for or supplement funds from DOE or other sponsors. LDRD projects may not be used to prepare conceptual design reports, or to fund construction line-item projects, facility maintenance, or capital expenditures of a general purpose nature.

LDRD PROGRAM PROPOSAL FORM

(Cover page to be attached to each proposal submitted to Strategic Planning Office)

PROJECT TITLE:

PRINCIPAL INVESTIGATOR(S):

ANL DIVISION(S) OR PROGRAM(S):

ALD OFFICE:

PRIOR FUNDING:
FUTURE FUNDING:

PROPOSAL CONTENT:
(Attached proposal format incorporates these and only these elements)

PURPOSE:
(Statement of the nature and purpose of the project)

WORK SCOPE:
(Delineation by reference of principal types of activities to be carried out. Taken together with the "purpose" paragraph, this should give enough detail so that a non-specialist will fully understand intent and scope.)

BACKGROUND:
(Description of technical/scientific opportunity or need)

BRIEF PROJECT SUMMARY:

(Description of scientific/technical activities named in the WORK SCOPE including anticipated approach, tools, etc.)

JUSTIFICATION:

(Estimation of likely scientific/technical benefits and potential for follow-on research support)

BUDGET AND EFFORT:

(Budget & effort plan)

ESTIMATE OF COMPARATIVE CONTRIBUTION TO LDRD PROGRAM OBJECTIVES:

Development of a novel R&D idea	_____%
Development of a new lab capability	_____%
Advancement of Laboratory R&D strategy	_____%
TOTAL:	100%

LDRD PROGRAM
PROPOSAL EVALUATION FORM

Project Title: _____

P.I./Division: _____

		Yes	No	Unknown
(1)	Will this funding be used to initiate a new project which is beyond the exploratory phase?	___	___	___
(2)	Will this funding be used to substitute for or increase funding for tasks normally funded by DOE or other users of the Laboratory?	___	___	___
(3)	Will this allocation create an implicit commitment of multiyear funding by initiating projects which will require significant funding in future years to reach a useful stage of completion?	___	___	___
(4)	Will this allocation be used to fund construction design (conceptual design, Title I, or more advanced design): or	___	___	___
(5)	Fund construction line-item projects, in whole or in part; or	___	___	___
(6)	Fund facility maintenance; or	___	___	___
(7)	Fund capital expenditures of a general purpose nature?	___	___	___

Reviewer's Evaluation/Judgment of proposal: (Circle) **(Must be completed or proposal will be returned)**

Scientific/Technical Merit:	Outstanding	Good	Adequate	Marginal	Poor
Relatedness to Lab Strategy:	Outstanding	Good	Adequate	Marginal	Poor
Innovative Appeal/Exploratory Nature:	Outstanding	Good	Adequate	Marginal	Poor
Expected Contribution to Science/Engineering Advance:	Outstanding	Good	Adequate	Marginal	Poor
Prospects for Future Support:	Outstanding	Good	Adequate	Marginal	Poor

Other Comments: _____

_____

_____

_____

_____

_____

1992 Annual Report

Argonne National Laboratory
Laboratory Directed Research and Development Program

FIVE YEAR FUNDING SUMMARY

Proposal No.	1990	1991	1992	1993*	1994*	TOTAL
92-006	-0-	-0-	97.9K	-0-	-0-	97.9K
92-021	-0-	-0-	95.2K	-0-	-0-	95.2K
92-022	-0-	-0-	180.4K	714.0K	500.0K	1,394.4K
92-024	-0-	-0-	70.0K	-0-	-0-	70.0K
92-031	-0-	-0-	128.5K	-0-	-0-	128.5K
92-044	-0-	-0-	200.8K	-0-	-0-	200.8K
91-025R1	-0-	175.4K	213.3K	149.0K	-0-	537.7K
92-162	-0-	-0-	238.8K	181.0K	125.0K	544.8K
90-001R2(a)	389.6K	514.1K	196.0K	-0-	-0-	1,099.7K
92-166	-0-	-0-	72.5K	-0-	-0-	72.5K
90-015R2	156.3K	187.5K	351.3K	-0-	-0-	695.1K
91-002R1	-0-	211.2K	210.0K	160.0K	-0-	581.2K
92-003	-0-	-0-	188.1K	150.0K	150.0K	488.1K
90-001R2(b)	-0-†	295.5K	102.0K	-0-	-0-	397.5K
92-110	-0-	-0-	47.5K	-0-	-0-	47.5K
90-001R2(c)	-0-†	-0-†	196.0K	-0-	-0-	196.0K
91-022R1	-0-	306.0K	288.0K	350.0K	-0-	944.0K
92-041	-0-	-0-	195.3K	210.0K	100.0K	505.3K
92-047	-0-	-0-	164.6K	125.0K	150.0K	439.6K
92-048	-0-	-0-	285.3K	-0-	-0-	285.3K
92-052	-0-	-0-	191.8K	-0-	-0-	191.8K
91-105R1	-0-	247.2K	204.3K	-0-	-0-	451.5K
92-177	-0-	-0-	215.7K	230.0K	-0-	445.7K
92-004	-0-	-0-	151.5K	140.0K	140.0K	431.5K

Proposal No.	1990	1991	1992	1993*	1994*	TOTAL
92-023	-0-	-0-	153.1K	120.0K	75.0K	348.1K
92-045	-0-	-0-	243.3K	200.0K	-0-	443.3K
91-016R1	-0-	247.5K	140.0K	-0-	-0-	387.5K
91-039R1	-0-	28.6K	54.0K	-0-	-0-	82.6K
92-179	-0-	-0-	99.0K	-0-	-0-	99.0K
92-008	-0-	-0-	99.0K	-0-	-0-	99.0K
92-012	-0-	-0-	106.6K	140.0K	100.0K	346.6K
91-038R1	-0-	37.0K	170.0K	140.0K	-0-	347.0K
91-037R1	-0-	32.1K	147.6K	-0-	-0-	179.7K
91-036R1	-0-	31.6K	159.3K	-0-	-0-	190.9K
92-016	-0-	-0-	101.9K	-0-	-0-	101.9K
92-109	-0-	-0-	298.4K	-0-	-0-	298.4K
91-012R1	-0-	300.1K	267.0K	95.0K	-0-	662.1K
92-108	-0-	-0-	242.1K	-0-	-0-	242.1K
92-113	-0-	-0-	110.1K	85.0K	-0-	195.1K
92-160	-0-	-0-	329.5K	305.0K	315.0K	949.5K
92-167	-0-	-0-	25.0K	-0-	-0-	25.0K
92-169	-0-	-0-	36.1K	-0-	-0-	36.1K
92-173	-0-	-0-	40.5K	-0-	-0-	40.5K
92-180	-0-	-0-	47.5K	195.0K	267.0K	509.5K
92-043	-0-	-0-	123.3K	100.0K	100.0K	323.3K
91-010R1	-0-	313.0K	265.1K	-0-	-0-	578.1K
92-172	-0-	-0-	49.1K	-0-	-0-	49.1K
92-181	-0-	-0-	65.0K	-0-	-0-	65.0K
92-042	-0-	-0-	121.4K	-0-	-0-	121.4K
92-049	-0-	-0-	192.3K	-0-	-0-	192.3K
92-053	-0-	-0-	198.6K	-0-	-0-	198.6K
92-168	-0-	-0-	125.6K	-0-	-0-	125.6K
92-171	-0-	-0-	16.2K	28.0K	-0-	44.2K

Proposal No.	1990	1991	1992	1993*	1994*	TOTAL
92-175	-0-	-0-	106.1K	200.0K	200.0K	506.1K
92-011	-0-	-0-	70.8K	-0-	-0-	70.8K
92-046	-0-	-0-	192.5K	-0-	-0-	192.5K
92-165	-0-	-0-	72.5K	-0-	-0-	72.5K
90-007R2	169.5K	256.1K	106.6K	-0-	-0-	532.2K
TOTAL:	715.4K	3,182.9K	8,859.9K	4,017.0K	2,222.0K	18,997.2

* 1993 and 1994 figures represent estimates and not actual expenditures.
† Included in 90-001R2(a).

92-006 -- DEVELOPMENT OF GENERAL PURPOSE X-RAY SHUTTER FOR APS

Associate Laboratory Director Area: Physical Research

Principal Investigator: J. R. Norris, Chemistry
L. Chen, Chemistry
M. K. Bowman, Chemistry
J. Tang, Chemistry
M. C. Thurnauer, Chemistry

Funding History: FY 1990 $0K[1]
FY 1991 $0K[1]
FY 1992 $97.9K
FY 1993 $0K
FY 1994 $0K

Purpose: We intend to develop an X-ray shutter for use on the APS which will select a single X-ray pulse from the synchrotron so that experiments can be conducted that exploit the 50 picosecond pulse width of APS for time domain measurements. It is necessary to be able to select a single pulse at will so that processes initiated by an external stimulus such as a laser can be examined and so that the sample can return to its starting state if pump-probe experiments are being conducted.

Approach: Experiments that exploit the structure of the APS X-ray beam require a shutter that can reduce the repetition rate of the X-ray pulses (a pulse every 177 nanoseconds) to match the repetition rate of an external stimulus (perhaps milliseconds or seconds) or to match the recovery or replacement of the sample (microseconds to minutes) depending on the process being studied on the APS.

A conventional mechanical chopper appears impractical because the shutter blade would be required to move at least four times the speed of sound even under the best conditions (single bunch mode). Our design is based on reflecting rather than blocking the X-rays.

In our design, an X-ray reflector will be spun rapidly. The reflected X-ray beam will be swept past a slit located two meters away. Since the X-ray beam has no mass, there are no problems in moving the beam much faster than the speed of sound even though it is equivalent to moving a mechanical chopper that is four meters in diameter. If the mirror which will be a facet on the

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[1]This work was supported under what is now LDRD project: "Picosecond Time Domain Studies Using Synchrotron Radiation"

side of a 4-5 inch rotor is rotated at a carefully controlled speed, we can select a single pulse between 100 and 1000 times each second.

Technical Progress and Results: We have refined the specifications for the shutter and have identified vendors with the capability to manufacture the needed components.

In brief, the shutter is envisioned as consisting of a rotor four inches in diameter with six sides, one of which will reflect X-rays. The rotor will be spun at nearly 15000 rpm with its speed phase locked to the orbit of the positron bunches in the synchrotron. The phase of the rotor's rotation will be adjusted so a single X-ray pulse will pass through a 0.5 mm slit located two meters from the rotor. The rotor must be at the correct position to within 8 nanoseconds if the center of the beam in the slit is to deviate by no more than 0.1 mm.

These requirements can be met by Speedring Systems in Rochester Hills, MI. On a visit to the Speedring Systems facility, a production rotor was demonstrated that exceeded the speed and stability requirements by more than a factor of two.
The other critical part of the shutter is the X-ray mirror to be placed on one of the facets of the rotor. One possibility is to use a totally reflecting metal mirror of conventional design. It has the advantage of being highly reflective and broadband but requires a shallow grazing angle of incidence. This shallow angle requires a bigger rotor than we would like because the facet face must be bigger. This would increase the cost of the whole shutter and limit the material the rotor could be made from. A very strong, rigid, lightweight material such as solid beryllium would be needed so that the rotor would not deform or fail at speed.

Another alternative to a total external reflection mirror is a multilayer mirror composed of alternating layers of low and high Z material with thicknesses of about 100 Å. With such a mirror, the smaller rotor envisioned here could be used but only about 50% of the X-rays would be reflected. In addition, a bandwidth of about 10-20% could be achieved, so this multilayer mirror would be limited to experiments using monochromatic X-rays or the beam from the APS designed undulator. Ovonic Synthetic Materials in Troy, MI is willing to make such mirrors on the rotor and the APS plans to have a multilayer coating facility in house. The stability of multilayer mirrors at the beam intensities that will be present at APS is controversial and their lifetime under operating conditions is not well tested. Improvements in multilayer mirror technology between now and the time APS is commissioned may remove this uncertainty.

The exact design parameters for the mirror depend critically on the beamline parameters where the shutter will be used and on the type of experiments to be performed with it. Final implementation must wait until these issues are resolved.

Specific Accomplishments: A design concept for the X-ray shutter has been developed. The key components in the rotor and mirror are commercially available and vendors are willing to supply them to the needed specifications.

The performance of rotors similar to those needed for the shutter has been verified on a visit to a rotor manufacturer.

The concept of the rotor is being patented and has been described in the Review of Scientific Instruments.

Publications Include:

"A Shutter Design for Time Domain Studies using Synchrotron Radiation at the Advanced Photon Source", Norris, J. R., Bowman, M. K., Chen, L., Tang, J., Thurnauer, M. C., Knapp, G. S., and Montano, P. A., Rev. Sci. Instrum. 63, 1172-1175 (1992)

"Single-Bunch Synchrotron Shutter", Norris, J. R., Tang, J., Chen, L., and Thurnauer, M. C., Patent DOE Case No. S-71,161 - Disclosure No. ANL-IN-90-04, (1991)

92-021 -- SSC CALORIMETER CALIBRATION SYSTEM

Associate Laboratory Director Area:	Physical Research
Principal Investigator:	R. G. Wagner, High Energy Physics

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$ 95.2K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: The tile/fiber calorimeters proposed for the Solenoidal Detector Collaboration (SDC) detector for use at the Superconducting Supercollider require a stable calibration system to map the response of the tiles during calorimeter module construction, to set the initial gains of modules to common values, and to measure and correct the gain constant on a periodic basis. Radiation damage to the scintillator tiles and optical fiber readout will affect the systematic uncertainty in calorimeter energy measurements. Layer-by-layer correction for degradation of the scintillator tile response will be necessary to maintain the required resolution of the calorimeter. Radioactive sources provide the most stable way of monitoring tile response over the period of many years. This project seeks to determine the precision required for the radioactive source based calibration system, to develop a mechanical design for incorporating the source calibration into the fabrication of the modules, and to demonstrate the feasibility of performing the calibration during construction and operation of the calorimeters.

Approach: The High Energy Physics Division has previous experience with the development and use of radioactive source calibration systems for scintillator based calorimetry in the Collider Detector at Fermi National Accelerator Laboratory (CDF) experiment and in the ZEUS experiment at the HERA electron-proton collider in Hamburg, Germany. The two systems have had good success with setting the initial gains of the calorimeters to the required precision. In the case of the CDF experiment, the source calibration system has tracked the response of the calorimeter for nearly a decade and has been used during this time as the primary measurement for correcting the energy response constants applied to the data before analysis.

Our study has used this background experience to identify the strengths and weaknesses of these calibration systems. We have incorporated into the SDC calibration design those features of previous systems that worked well. We have attempted to develop the design to avoid the problems encountered with the previous systems.

Compactness and limited space within the calorimeter were the most important mechanical constraints on the design. We have worked with the design engineers and with physicists from collaborating institutions on a design that incorporates the guide tubes for the radioactive sources into the lead absorber plates of the electromagnetic calorimeter. Our collaborators include Virgil Barnes and Changzhan Zhao from Purdue University and Craig Blocker from the SSC

Laboratory. Norm Hill, a High Energy Physics Division engineer, worked extensively on the mechanical design of the system. This design required demonstration by calculation and subsequent experiment that the tubes could be located within the lead absorber accurately enough on a module-to-module basis. Don Jankowski, Dave Lopiano, and Bob Stanek, of the High Energy Physics Division, measured the effect of tube location in the lead on the response from source irradiation.

Technical Progress and Results: We have demonstrated a prototype calibration system on two electromagnetic calorimeter test modules that were fabricated to demonstrate the feasibility of the tile/fiber calorimeter. Each module consisted of ten calorimeter towers arranged in a configuration of five towers in polar angle by two towers in azimuth. Source tubes were incorporated into the modules during the casting of the lead plates. We have developed a computer automated system to insert the source into any of the many source tubes contained in the modules and to measure the response of the calorimeter at several of the layers by the current produced in the photomultiplier tubes used to readout the calorimeter. Radioactive source scans have also been done along the radial length of towers using tubes attached to the outside of the calorimeter for this purpose.

We have begun a program to determine the extent to which the radiation environment at the SSC will degrade the response of the calorimeter. We have used the ^{60}Co irradiation facility and the JANUS reactor neutron facility within the Biological and Medical Research Division at Argonne to irradiate scintillator tile samples and measure the diminution of response and its subsequent recovery. We have procured, through this LDRD project, radiochromic film and an optical density measuring machine to provide an accurate measure of radiation fluences for these irradiations. This work is being carried on by Don Jankowski.

During the year we automated control of the source and performance of the digitization of the current signal from the calorimeter phototubes. Software was developed and installed to handle readout and display of the current response. We have attached guide tubes radially along the test calorimeters and have performed source run tests both radially and along the polar direction of the calorimeter.

The calculations and measurements performed to determine the effect of source tube location within the lead on the response indicates that the tolerance that can be achieved during fabrication (0.25 mm) is sufficient for the accuracy required of the source calibration. We have shown in calculations that the effect of source tube mislocation nearly subtracts out in extracting a layer-by-layer response. Moreover, Craig Blocker at the SSC Laboratory has found that a pairwise extraction of response greatly simplifies the layer-by-layer response determination.

Calibrations have been performed on the radiochromic film and we now have a method to determine radiation fluences to the accuracy of a few percent. We anticipate this will result in much improved measurements of radiation damage effects.

Specific Accomplishments: We have to date published one SDC technical note on the source

tube location measurements. The design developed for the calibration system has been incorporated into a full-scale prototype. The prototype will be tested in a particle beam and the absolute response calibration will be tracked with the radioactive source system.

Publication: "Effect of Pb and Air Absorber Thickness on ^{137}Cs Signal," D. Jankowski, D. Lopiano, and R. Stanek, ANL-HEP-TR-92-97 and SDC 92-350.

92-022 -- FEASIBILITY STUDY FOR THE PULSED NEUTRON RESEARCH FACILITY (PNRF)

Associate Laboratory Director Area: Physical Research

Principal Investigator: B. S. Brown, Intense Pulsed Neutron Source
J. M. Carpenter, Intense Pulsed Neutron Source
Y. Cho, Advanced Photon Source

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$180.4K
FY 1993	$714K
FY 1994	$500K

Purpose: ANL has been a pioneer in development and utilization of accelerator based pulsed neutron sources. The purpose of this study is to update recent developments from around the world, and to develop an up-to-date design for future consideration. Construction of such a facility at a future date could be one of the major initiatives for the Laboratory.

Approach: Approximately ten years ago, ANL personnel had designed various accelerator scenarios for high flux spallation sources. However, following the recommendation of 1984 of the Seitz-Eastman Committee of the National Academy of Sciences, which placed the pulsed source option behind the Advanced Neutron Source (reactor) in priority, the pulsed source study activities have been dormant. About one year ago, European colleagues invited several ANL spallation source experts (on accelerators, neutron generating targets and neutron scattering) to meetings to discuss design activities for a 5 MW European Spallation Source (ESS). At the same time, it was thought that it was the right time to revisit spallation source concepts in general and, in particular, a site specific design utilizing available infrastructure of the former Zero Gradient Synchrotron (ZGS) complex.

It was felt by the personnel working on this topic that designing a 5 MW source like ESS would be too big of a jump from the existing technology, and the goal was set to study some intermediate level source with an open option of going to higher power at a later date. In 1983, ANL staff had published a design on a 550 kW, rapid cycling synchrotron (ANL 83-13). The contents of this publication are the starting point of present work.

Personnel involved in the past year's work on the accelerator design concepts were: R. Kustom, E. Lesner, W. McDowell, D. McGhee, F. Mills, R. Nielsen, T. Rauchas, and K. Thompson.

It was also thought necessary to perform calculations and design studies on target systems for the higher power accelerator. The work on the targets and moderators was led by J. Carpenter and performed by D. W. Jerng, a post-doc hired for this purpose.

Technical Progress and Results: Exchanges of ideas between the accelerator personnel and neutron scattering instrumentation scientists determined that a 30 Hz pulse repetition rate is desirable to avoid signal frame overlap. This is different from the 50 Hz ESS concept. Another conclusion made from the discussions with the instrumentation scientists is to design two independent target stations, thereby doubling the number of beam lines available. One station is to handle 10 Hz operation and the other 20 Hz.

Taking these considerations into account, the initial accelerator system study resulted in a conceptual layout of a 750 kW, 30 Hz synchrotron, which can be placed within the existing ZGS ring building with one target in Building 369 and the other in Building 370. The synchrotron is to accelerate protons from 400 MeV to 1.5 GeV. The number of protons accelerated per pulse is about 1×10^{14}.

Using the conceptual parameters of performance and hardware, the staff performed bottoms-up cost estimates of the technical components. The Advanced Photon Source Project's data base on the components costs was used to do this task.

Work performed so far set the scope of the study, and what follows in FY93 will optimize and refine the design of the accelerator system. Some optimization has already started: a detailed inspection of the machine layout shows that the synchrotron energy can be raised from 1.5 to 2.2 GeV, which results in a beam power of 1.1 MW.

The first phases of the target work focused on specifying a computer system needed for the target system studies. After surveying our resources and needs, we used a Sun work station and obtained codes, data libraries and documentation for high-energy nucleon transport and low energy neutron transport calculations, at the same time establishing lines of communication with other experts in other laboratories. The first work produced power density and neutron production information for highly idealized geometries and checked against reference calculations done by others. Work was begun on the establishment of progressively more detailed geometric models and the calculation of power densities, neutron production rates, neutron fluxes and beam currents from moderators.

Specific Accomplishments: A preliminary design has been developed and it was presented at DOE's BESAC Panel on Neutron Sources in September 1992. Results were presented at the Fifth International Topical Meeting on Nuclear Reactor Thermal Hydraulics in September, 1992.

92-024 -- DEVELOPMENT OF SECONDARY BEAMS AT ATLAS FOR NUCLEAR ASTROPHYSICS

Associate Laboratory Director Area:	Physical Research
Principal Investigator:	W. Kutschera, Physics K. E. Rehm, Physics J. P. Schiffer, Physics

Funding History:		
	FY 1990	$ 0K
	FY 1991	$ 0K
	FY 1992	$ 70K
	FY 1993	$ 0K
	FY 1994	$ 0K

Purpose: Development of the capability of ATLAS to produce beams of short-lived radioactive isotopes for nuclear reaction experiments. The objective is to produce secondary beams of variable energy and sufficient intensity for studying nuclear reactions believed to contribute significantly to the synthesis of light elements (up to ^{40}Ca) under "hot" stellar conditions. In such an environment, nuclear reactions start to compete with beta decay of radioisotopes, even if they are short-lived. ATLAS provides unique opportunities for such a program.

Approach: A short-lived secondary beam is produced in a nuclear reaction with a primary beam half-way through ATLAS. The secondary particles are refocussed and accelerated or slowed down in the second half of ATLAS to the energy required for the specific reaction to be studied. The basic principle has been tested with a primary beam of ^{17}O on a hydrogen target producing the short-lived radioisotope ^{17}F ($t_{1/2}$ = 64 sec) via the reaction $^{17}O + H \rightarrow {}^{17}F + n$. The major technical challenge is to develop a system which produces sufficient secondary-beam intensity for studying nuclear reactions. Development in three different areas are required to achieve the projected goal for a secondary beam intensity of ten million (10^7) particles per second: (i) the development of a rotating hydrogen target which can stand primary beams of high brilliance, (ii) beam optics calculations to determine the best location for this target, and (iii) strong beam-focussing lenses immediately before and after the rotating target to generate the high-brilliance primary beam and to refocus the diverging secondary beam. This project concentrated on points (i) and (ii). Additional participants in this work include Tzu Fang Wang from Lawrence Livermore National Laboratory who contributes his expertise in nuclear astrophysics, Richard Pardo who is the operations manager of ATLAS and an expert in beam optics calculation, and Dan Berkovits, a graduate student from the Hebrew University Jerusalem who was instrumentalin building and testing the rotating target assembly.

Technical Progress and Results: Extensive beam optics calculation with a RAYTRACE program were performed on a PC (486). Both longitudinal and transverse emittance phase space of the secondary particles were traced through the accelerator system. As a result of these calculations it was concluded that the best position for the secondary-beam production target would be as

close as possible to the entrance of the second part of the superconducting linac. In this way the existing first superconducting solenoid in the linac can be used for refocussing the secondary beam particles. The other major development in FY92 was the construction and testing of a rotating target. A solid hydrogen target consisting of aluminum coated polypropylene foils, whose basic building blocks are CH_2 chains, was shaped into 8-cm disks and rotated up to 3000 rpm in a special vacuum chamber mounted at a beamline of ATLAS. With this system a hundred-fold higher primary beam intensity could be accepted as compared to a stationary target. Altogether, the rotating target performed very successfully in the beam tests with high-intensity beams of 50-MeV ^{19}F. After these tests, modification of the rotating target chamber were implemented to adapt it for installation in the desired target position at ATLAS. Beam time has been requested at ATLAS to perform a crucial test before the chamber will be installed in its final position at ATLAS. The full system will then be tested. The result of this test will determine a possible upgrading of the system with a superconducting solenoid for a tighter focussing of the primary beam onto the rotating hydrogen target. Funds have been requested from DOE for FY93 and FY94 to continue the project along these lines.

Specific Accomplishments: The development of this project has generated considerable interest in the nuclear physics community, which in its recent long-range plan[1] has expressed intense interest for beams of radioactive isotopes. This is expressed in an invited talk by Walter Kutschera entitled "Production of a Variable-Energy Radioactive Beam with One Accelerator" at the Twelfth International Conference on the Application of Accelerators in Research and Industry, University of North Texas, Denton, November 2-5, 1992.

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[1] "*Nuclei, Nucleons, Quarks: Nuclear Science in the 1990s, A Long Range Plan by the DOE - NSF Nuclear Science Advisory Committee, December, 1989*," U.S. Department of Energy, Office of Nuclear Physics and Division of Nuclear Physics, National Science Foundation.

92-031 -- A PARTIAL SNAKE FOR POLARIZED PROTON BEAMS

Associate Laboratory Director Area: Physical Research

Principal Investigators: D. G. Underwood, High Energy Physics
A. Yokosawa, High Energy Physics

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$128.5K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: We want to insure the technical feasibility of the use of a spin precession snake to preserve polarization during acceleration of protons to high energy for the first time. The concept has only been tested previously in a non-accelerated situation at low energy. If successful, this will allow the use of high intensity-high energy polarized beams in general, and specifically it will facilitate spin physics at the Relativistic Heavy Ion Collider (RHIC). Our group in ANL-HEP is proposing a program of studies that will depend upon polarized protons in RHIC.

Approach: The basic problem with preserving the polarization of protons during acceleration is depolarizing resonances. There are two kinds of such resonances. Imperfection resonances are due to imperfections in the accelerator that involve horizontal magnetic field components. Intrinsic resonances are due to the focusing fields and the vertical motion of the particles about the central orbit. A so-called full snake can eliminate both kinds of resonances by flipping the polarization 180 degrees on each turn, so that perturbations are self-canceling at the resonance. A full snake will not fit into a typical accelerator like the Alternating Gradiant Synchrotron (AGS) and would also disturb the beam excessively below about 50 GeV. A partial snake precesses the spin by a smaller amount such as 9 degrees. This is calculated to give cancellation of the intrinsic resonances.

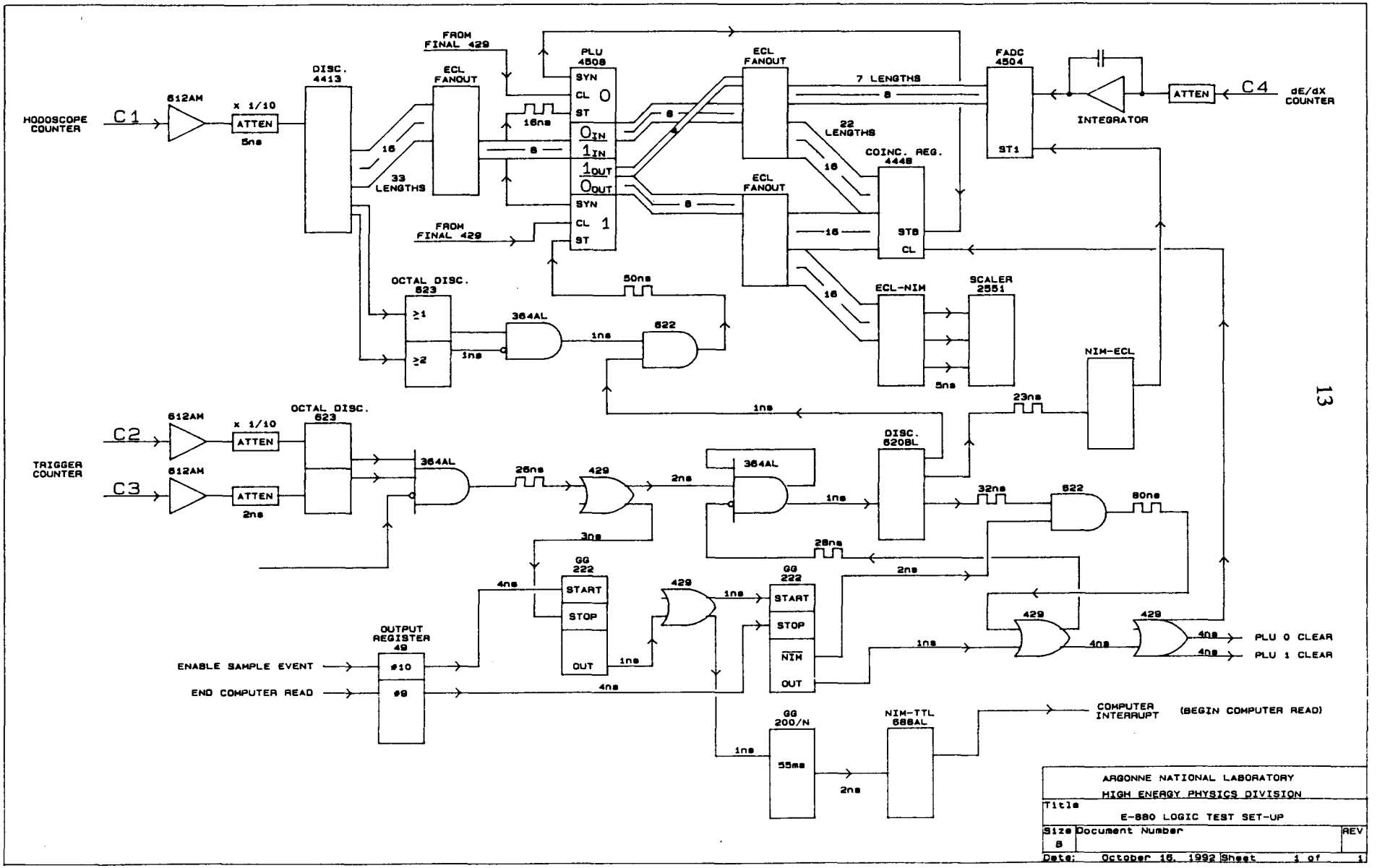
We investigated many designs for both the snake solenoid magnet and the polarimeter to measure the beam polarization. In order to determine whether the partial snake is effective, a polarimeter is needed. This polarimeter must measure the absolute beam polarization over a broad range of energy. It must function with an internal target in the accelerator and with no extraction of the beam. This last requirement is both to make the testing economically affordable and to obtain enough interactions to measure the polarization quickly for a series of many tests.

The magnet for the partial snake is an air core solenoid so that it can ramp to full field in phase with the acceleration process in about 1 second. Even at 10000 Amperes the spin will be precessed only 9 degrees around the beam axis. The magnet itself is a joint effort of Argonne, Indiana U., Triumf, and Brookhaven.

ANL-HEP has responsibility for the polarimeter system. Contributions to the magnet design and construction were also made.

Technical Progress and Results: A methodology for the polarimeter was chosen on the basis of studies of three different approaches. The studies involved Monte-Carlo simulation of the physics response, partial electronics designs, and consultations on the level of technical difficulty. The Monte-Carlo studies were done by H. Spinka and D. Underwood. A working fast electronics system was set up and tested for half the polarimeter. The electronics system was set up by Rebecca Surman and D. Underwood (Figure 1). Several tests were conducted in vacuum for a prototype data system of the internal target and a prototype motion system was assembled. The core subroutines for a data acquisition system were written and debugged using real electronics and signals. A model of the detector was constructed to insure feasibility (Figure 2).

Specific Accomplishments: We believe we have established the technical feasibility of a realistic partial snake experiment. Two Undergraduate students did summer projects related to this work, coordinated by Argonne Division of Educational Programs. A paper was written: "Progress on Aspects of the AGS E-880 Internal Polarimeter" by Rebecca Surman, State University of New York at Geneseo. This work has attracted several more physicists to work on accelerator and physics experiments which may be possible because of this project.



ARGONNE NATIONAL LABORATORY HIGH ENERGY PHYSICS DIVISION		
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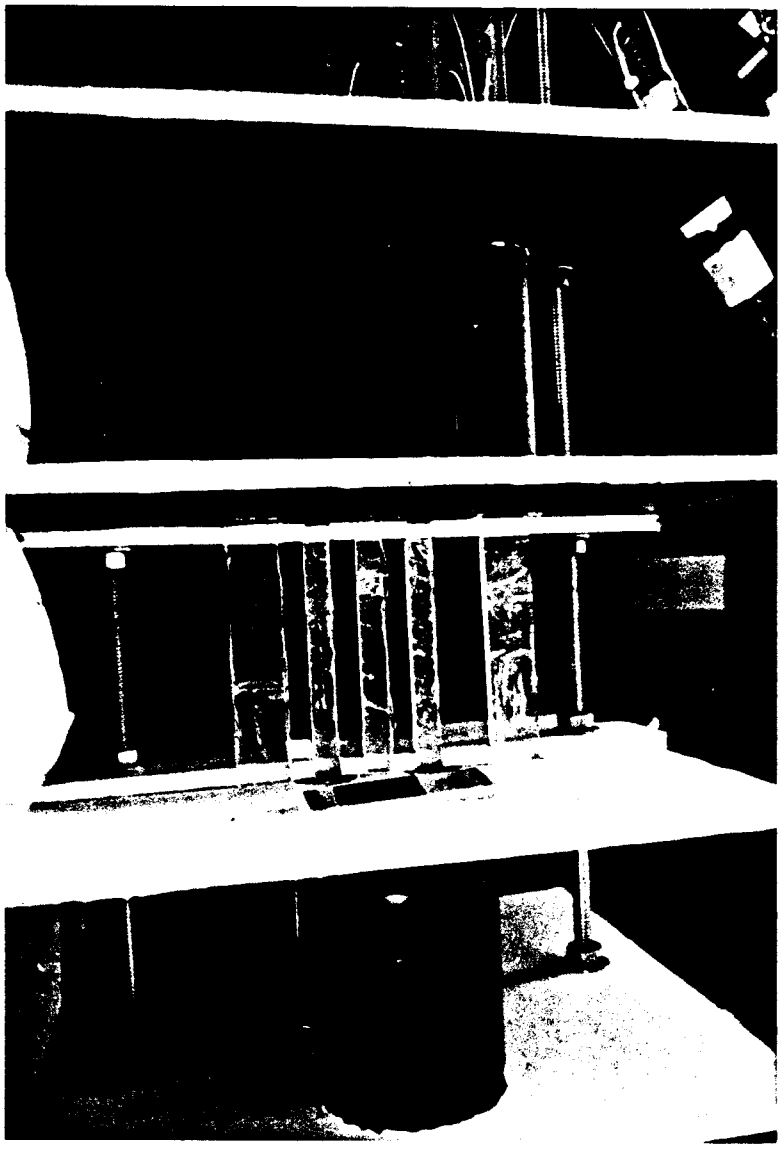


Figure 2: Photograph of Polarimeter Detector

The active components of the polarimeter recoil arm detector were assembled within a temporary support structure. This was useful for determining the closest placement of components, the cable routing, and the size of the magnetic shield.

92-044 -- SUPERCONDUCTING STRUCTURE FOR ACCELERATION OF HIGH-CURRENT ION BEAMS

Associate Laboratory Director Area: Engineering Research

Principal Investigator: J.R. Delayen

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$200.8K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: To design, build and test and the first superconducting accelerating structure to be used to accelerate a high-current ion beam. While superconducting accelerators offer many distinct advantages for high-current ion beams, the fact that no such demonstration has taken place because of the nonexistence of such a beam has often been used as a reason to ignore superconducting accelerators and concentrate on normal conducting accelerators. The experiment which we proposed would lead to this demonstration and remove one of the final roadblocks in the acceptance of the superconducting technology, and will confirm and extend ANL leadership in the technology of high-current cw ion accelerators.

Approach: The number of applications for high-current ion beams is rapidly increasing. Until now the accelerators which have been proposed for these applications involve the use of normal conducting copper structures. As the conceptual designs of these accelerators are studied in more depth it is becoming apparent that the use of normal conducting structures will pose some very serious problems of heat removal, power efficiency, and activation.

For several years, the EP Division at ANL has promoted the use of superconducting structures for these accelerators and great progress has been made experimentally and theoretically. However, in spite of these achievements which have been recognized in the accelerator community, there is a reluctance to accept the use of superconductiong structures for high-cuurent ion beams because such use has never been demonstrated. This demonstration would remove one of the final objections which have been raised against the use of superconducting accelerators for high-current ion beams. Until recently, this demonstration was not possible since no suitable beam was available.

During the summer of 1991, the Chalk River National Laboratory successfully operated Radio Frequency Quadrupole (RFQ) which produces 25 mA of protons at an energy of 1.2MeV. This is the first high-current cw ion beam which is available for testing a superconducting accelerating structure, and the Accelerator Group at CRNL has offered the use of that facility for testing one of our structures.

The proposed research would consist of several parts spanning several years.

- First a design of the whole experiment and all its parts would take place: matching to the RFQ, superconducting cavity, cryostat, control electronics, rf power source and coupler, tuner, focusing elements, etc. This phase of the program would take place in close collaboration with the CRNL group.
- Second, the superconducting cavity and the cryostat would be built and tested without beam at ANL.
- Third, the cavity would be tested with beam at Chalk River.

Additional participants in this research included, C.L. Bohn, W.L. Kennedy, G. Nicholls, C.T. Roche and L. Sagalovsky from the EP Division at ANL. The collaborators from the Chalk River Laboratory included G. Arbique, M.S. de Jong, R. Hutcheon, G.E. McMichael and J.Y. Sheikh.

Technical Progress and Results: All the objectives for the first year consistent with the level of funding have been achieved. The complete experiment has been defined and its parts have been designed. This included close collaboration with CRNL to define and design the matching section between their RFQ and our cavity. The cavity geometry has also be selected and the cavity designed. Because of the very low beam velocity, the cavity geometry is novel in that it is a quarter-wave structure with a 3/2 $\beta\lambda$ distance between the gaps as opposed to the usual 1/2 $\beta\lambda$. The experiment and the design were reviewed at a joint meeting between ANL and CRNL were they were approved together with a schedule for the remainder of the joint effort. A schematic of the cavity, the cryostat, and the high-power coupler are shown in the attached drawing (Figure 1).

While the proposed research has accomplished its design phase, it does not seem likely that it will proceed through the construction and experimental phase as originally intended since it was announced during the spring of 1992 that the ion accelerator program at Chalk River will be terminated.

Specific Accomplishments: The experiment and its design have been presented in a paper: "Research and Development of Superconducting Linear Accelerators for Neutral Particle Beam Applications". Proceedings of the 1992 NPB Symposium and Technical Interchange.

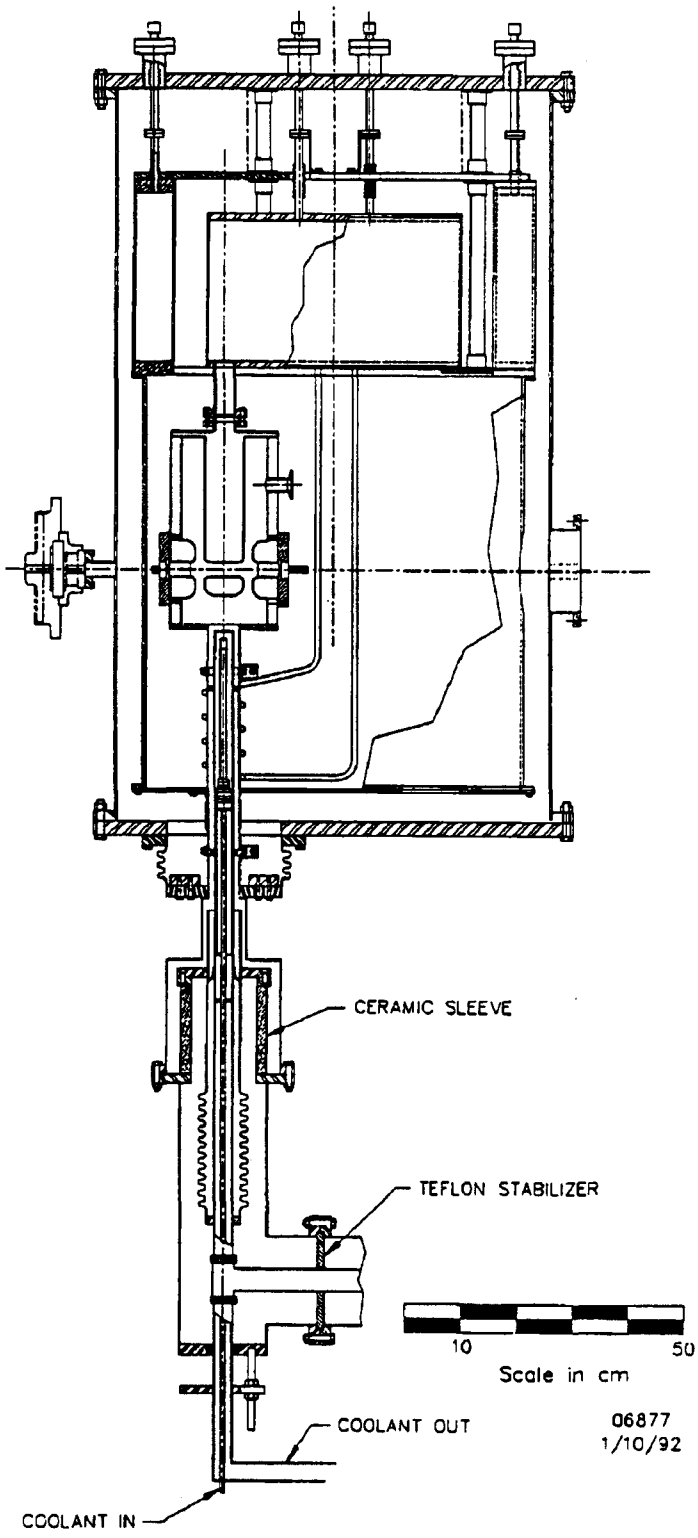


Figure 1. Schematics of the proposed experiment to test a superconducting cavity at the exit of RFQ-1250 at Chalk River Nuclear Laboratory.

91-025R1 -- PRODUCTION AND STUDY OF COHERENT RADIATION USING THE ADVANCED PHOTON SOURCE (APS) LINAC

Associate Laboratory Director Area:	Advanced Photon Source
Principal Investigators:	G. Mavrogenes, Accelerator Systems M. Borland, Accelerator System E. Gluskin, Experimental Facilities

Funding History:

FY 1990	$ 0K
FY 1991	$175.4K
FY 1992	$213.3K
FY 1993	$149K
FY 1994	$ 0K*

Purpose: A test stand providing a low-emittance electron beam of the proper-energy offers the capability to readily assess the performance of novel insertion device (ID) designs. Such R&D serves to efficiently determine the most productive direction for future ID research and design.

Approach: There are several promising avenues for the enhancement of the spatial coherence of ID radiation. One of these involves the use of multi-section devices, such as a double-undulator system, where the two undulator sections are separated by an achromatic bend section. For this type of multi-sectioned device, a low emittance particle beam is essential, as is the preservation of that low emittance in a storage ring containing such an insertion device. Under favorable conditions, the radiation coherent phase-space area is expected to be at least a few orders of magnitude greater than that produced by a single planar undulator.

Another type of multi-undulator device has the potential to substantially improve the temporal coherence of X-ray radiation while simultaneously preserving the total power. This system is based on a set of identical undulators with dispersion sections between them, and produces a set of sharp X-ray lines inside the width of an undulator harmonic. The multi-undulator system selects one of these lines and, given a low emittance electron beam, can provide extremely high coherent radiation power.

While other systems are possible, the two proposed systems are representative of the types of new geometries that need to be investigated for the enhancement of coherent flux. Similar devices have also been proposed for the enhancement of polarization properties, and these could be of potential interest to the program. These devices are of multi-section design and result in complex perturbation of the particle beam.

Another area of potential interest is the production of 1 to 100 micron radiation using short electron bursts from an RF linac coupled with an undulator installed within resonant mirrors. The Advanced Photon Source (APS) will have a 650 MeV electron linac as part of the injector facilities, capable of accelerating up to 50 nC of charge in a 30 ns pulse. However, the emittance of this beam is too large to make it suitable for the applications proposed here.

The only available way of improving the beam emittance is to use a high-brightness, RF-gun-based system in place of the existing thermionic triode gun with its associated prebuncher. Use of a thermionic RF gun is a cost-effective way to provide an electron beam with emittance reduced by a factor of 15. Space is available for such a gun and its associated transport system in the region of the first section of the APS linac, with injection into the second linac section. Space is available to extract this beam into the infield region of the APS and for the construction of required experimental facilities.

Technical Progress and Results: A fully electromagnetic and relativistic particle-in-cell code (SPIFFE) was written for simulation of the RF guns with space charge. The code is able to simulate multi-cell structures, a requirement not satisfied by the MASK code, which was used previously. SPIFFE has extremely flexible post-processing and interfaces directly to the 6D tracking program ELEGANT, to allow simulation of the gun-to-linac transport line.

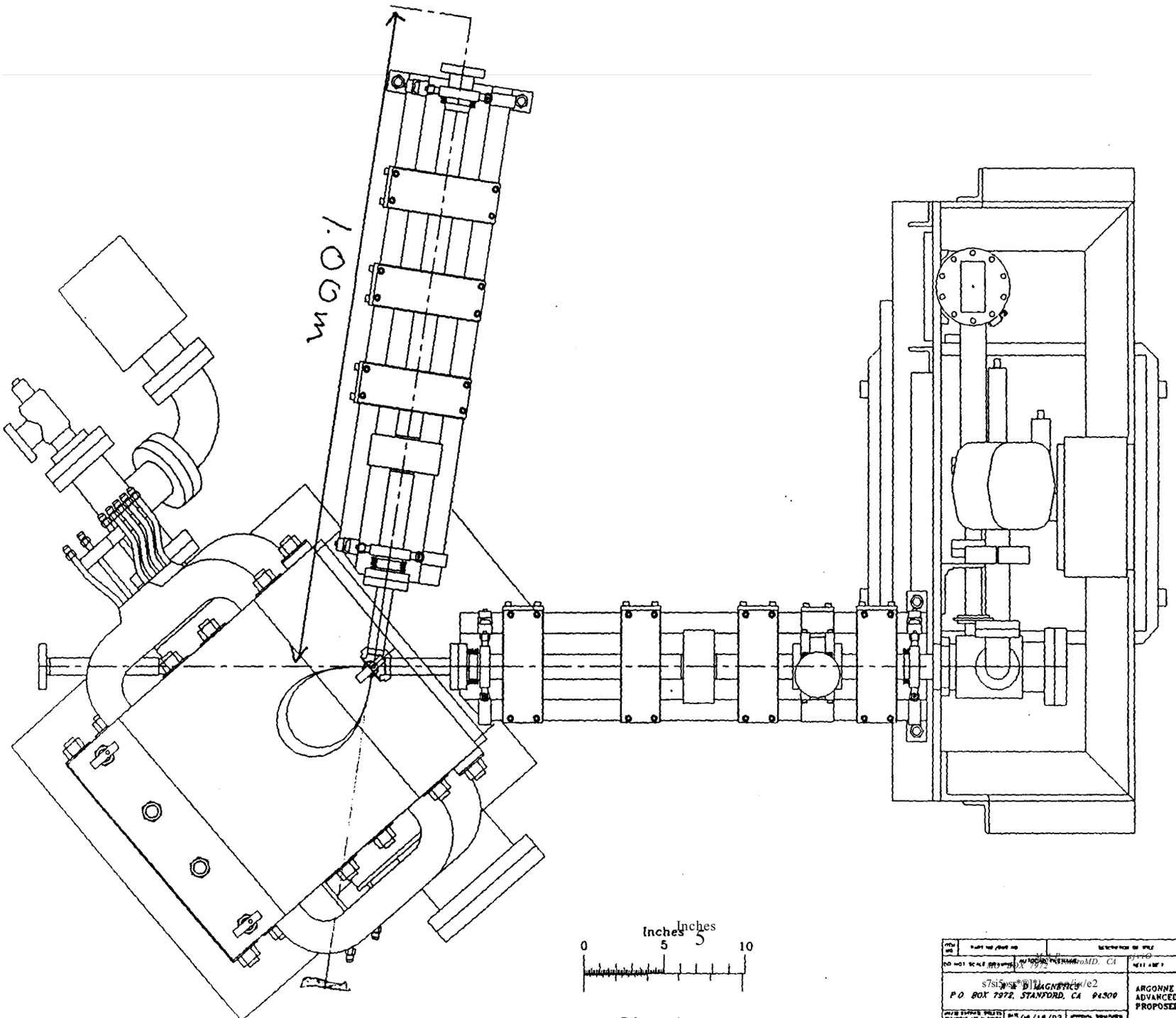
Design of the gun-to-linac transport line was completed. The transport line preserves the original emittance of the beam to within 20% for a wide range of gun energies, even in the presence of ±5% momentum spread (Fig. 1). A paper describing the transport line is in progress.

The utilization of the linac as a test-bed for various types of undulator geometry has been studied. As it was pointed out in the proposal the small emittance makes the linac an ideal source for evaluating undulator performance and its interaction with the particle beam. We have investigated the results of installation of the wedge-pole undulator that was recently used as the first device for the linac stand. The wedge-pole device has a magnetic period 3.3 cm, the same as Undulator A will have. The radiation spectrum of this device installed in the linac is represented in Fig. 2. There is almost negligible presence of even harmonics in this spectrum because of a very low linac emittance. As it follows from our calculations, an rms field error of 0.6% will degrade the third harmonic peak flux by 25% if installed on APS, while if it is installed on the linac, the peak flux will be decreased by 65%. This higher sensitivity is possible because the higher harmonic in the linac case (in this example the seventh harmonic vs. the third for APS, Fig. 3) was not deteriorated by the particle emittance and can be effectively utilized for spectral characterization. In another case, it was found that the linac beam can detect a dc field error of < 0.5 Gauss in the Undulator A type device.

Other areas considered include generating highly coherent X-ray beam for studying their coherence properties. The linac is a diffraction-limited source of X-rays at energy < 100eV. In the case of Undulator A, the first harmonic is at 30eV ($K = 2.17$) for the linac. Thus, both the fundamental and the third harmonic will be fully coherent, while the fifth and the seventh

harmonics are partially coherent. This provides a very good source for analyzing the coherence of X-rays and also testing of coherent optics. Another useful property of the linac is that the emittance can be adjusted to be identical in both horizontal and vertical direction. This results in a fully symmetric source of X-ray, and it greatly simplifies the analysis of the spectra.

Specific Accomplishments: Internal notes produced - M. Borland, "Summary of Equations and Methods Used in SPIFFE," Advanced Photon Source Internal Note APS/IN/LINAC/92-2, June 29, 1992. S. Xu and B. Lai, "APS Undulator and Wiggler Sources: Monte-Carlo Simulation," ANL/APS/TB-1, February, 1992.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10
ARGONNE NATIONAL LABORATORY
ADVANCED PHOTON SOURCE
PROPOSED GUN TO LINAC LAYOUT
P O BOX 7972, STANFORD, CA 94309
06/18/02

Fig. 1

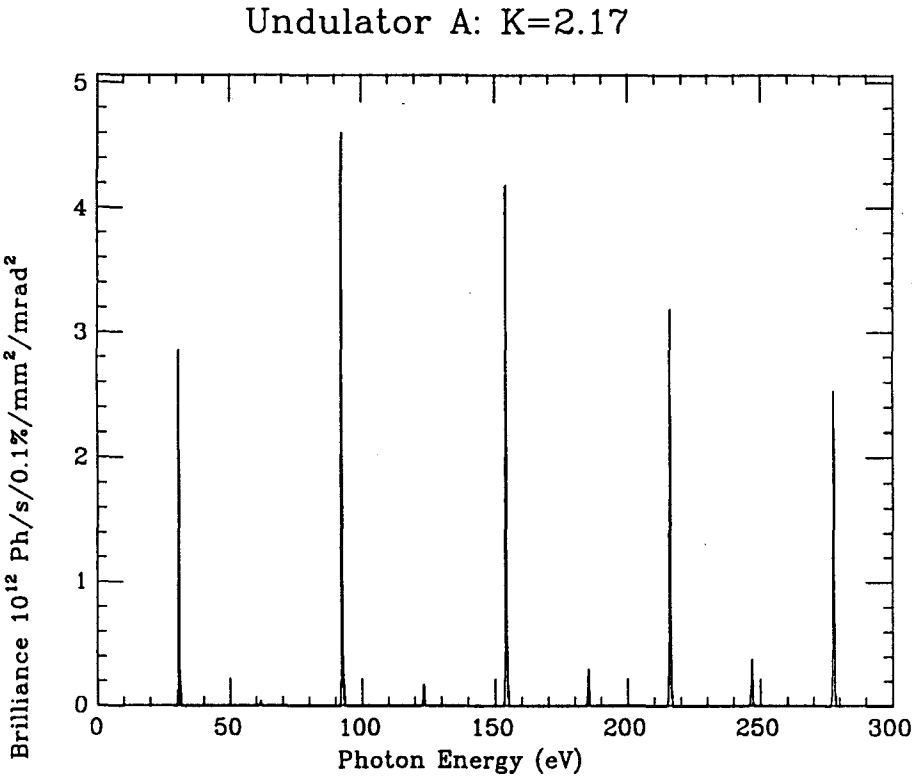

Undulator A: K=2.17
Brilliance 10^{12} Ph/s/0.1%/mm^2/mrad^2
0
1
2
3
4
5
0
50
100
150
200
250
300
Photon Energy (eV)

Fig. 2

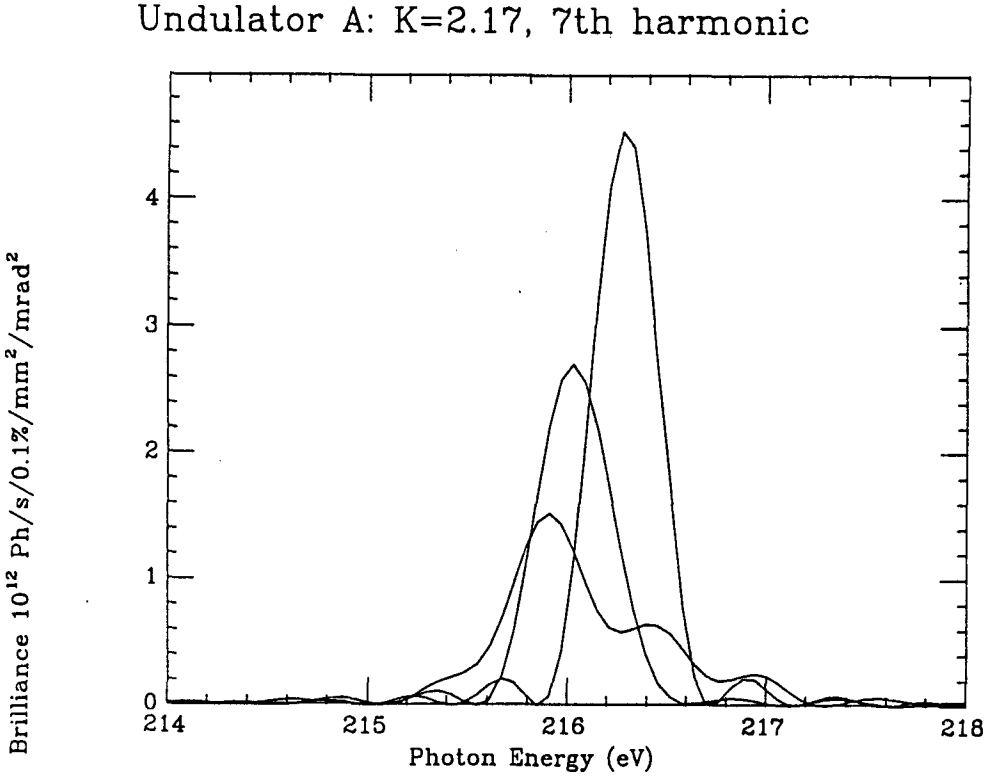

Undulator A: K=2.17, 7th harmonic
Brilliance 10^{12} Ph/s/0.1%/mm^2/mrad^2
0
1
2
3
4
214
215
216
217
218
Photon Energy (eV)

Fig. 3

92-162 -- THE INVESTIGATION OF NOVEL DETECTORS FOR ULTRA-FAST TIME-RESOLVED STUDIES USING SYNCHROTRON RADIATION

Associate Laboratory Director Area: Advanced Photon Source

Principal Investigators: Brian Rodricks, Experimental Facilities Division
Dennis Mills, Experimental Facilities Division

Funding Profile:

FY 1990	$ 0
FY 1991	$ 0
FY 1992	$238.8K
FY 1993	$181K
FY 1994	$125K

Purpose: To investigate the development of an advanced two-dimensional x-ray sensitive Pixel Array Detector (PAD), readout electronics, and state-of-the-art display for high-resolution time-resolved x-ray imaging applications. Currently, there are no position-sensitive detectors in the field of synchrotron radiation that are radiation hard and can be read out at high speed. Further, because of limited marketability, there are few commercial organizations investigating them. The objective of this program was to determine the feasibility of developing a novel position-sensitive pixel array detector that was both radiation hard and capable of high-speed readout and to initiate the development of a high-speed data acquisition system. Argonne National Laboratory is in the process of building the brightest synchrotron radiation source in the world, namely the Advanced Photon Source (APS). To take full advantage of the beam brightness, development of high-speed area detectors is critical. This LDRD program addresses the development of these advanced detectors.

Approach: Over the past twenty years, synchrotron radiation has been used extensively as a source of x-rays in the fields of physics, chemistry, biology, medicine, and others,[1] first in a parasitic mode at high energy physics facilities like at the Stanford Synchrotron Radiation Laboratory (SSRL) and the Cornell High Energy Synchrotron Source (CHESS), and then at dedicated facilities like the National Synchrotron Light Source (NSLS). At present, four ultra-high brilliance insertion-device-based third generation synchrotron sources, namely the Advanced Photon Source (APS), the Advanced Light Source (ALS), the European Synchrotron Radiation Facility (ESRF), and the Super Photon Ring (SPring) are in their construction phase. During this period of time, photon brilliance has increased many orders of magnitude[2] allowing the advance of established techniques and opening up new avenues of research. Unfortunately, during this remarkable pace of growth in beam brilliance, the research and development of detectors have not kept pace. A large percentage of forefront x-ray science is still done with scintillation detectors. In experiments where two-dimensional detectors are required, x-ray sensitive photographic film or imaging plates have been used. Charge coupled devices (CCDs) are being increasingly utilized where positional information

is required.[3] (There are numerous situations where positional information is necessary such as angiography, protein crystallography, x-ray holography, various transmission imaging studies, and time-resolved studies.) The advantages of charge couple devices (CCDs) over film or imaging plates are their high spatial resolution and low noise. The disadvantages are their limited dynamic range and a serial readout that is inherently slow.

No currently available area detectors have framing rates greater that 100 Hz. Pixel array detectors (PADs) have the potential to have framing rates approaching a megahertz and, hence, provide a marked improvement in high-speed area detector performance. There are two main aspects to the development of a practical PAD system. First, the pixel array chips must be fabricated. The chip fabrication part of the project is a joint collaboration with Prof. Sol Gruner and Prof. Peter Eisenberger of Princeton University. Princeton University brings to this project expertise in the manufacture of experimental detector chips. The second aspect is the development of a sophisticated flexible electronic readout system that allows us to first characterize the device and then control it in normal operation. The devices being fabricated are experimental devices, thus, the readout requirements will vary from device to device. Hence, to read-out the device and to optimize performance, we are developing a software programmable system. APS has considerable experience in the development of programmable readout systems for CCDs. This experience will be utilized to develop the readout for these experimental devices.

Knowing our requirements, we came up with a design for a PAD. This device would be fabricated by a silicon foundry and then tested at ANL.

Our design specifications had to satisfy the following requirements:

1) 1000 x 1000 pixel device
2) 100 μm square pixels
3) The detector must be radiation hard
4) The detector must be able to be read-out at high speed (~1-2μsecs/frame)
5) The detector must be 100% quantum efficient for x-rays up to 20keV

With these requirements, we decided on a 'bump bonded' hybrid device whereby the x-ray sensitive photodiode is connected to a CCD storage device by means of a blocking layer (Fig. 1 and Fig. 2).

For the readout electronics, we decided on a modular system based on the industrial standard VXI mainframe where modules from different high technology companies follow the same protocol and can be controlled from a single controller.

Technical Progress and Results: Substantive work on the project started following a planning meeting at ANL between APS and Princeton staff. The conceptual design evolved quickly to a workable scheme, estimates of the needed resources were determined, critical vendors were identified, and discussions with the High Energy Physics (HEP) community

familiar with PADs were used to help define the best route for success of the project.

High Energy Physics scientists recommended that we consult with SRI Sarnoff Laboratory of Princeton, New Jersey, because of their extensive CCD and electro-optics experience and a

history of custom integrated sensor package development. Contact was made with the electro-optics group at Sarnoff and, indeed, the PAD design evolved rapidly.

On the readout electronics side of the project, a postdoctoral scientist was hired to begin the design of the electronics system. The VXI based system, being state of the art, required extensive startup software and interaction with many commercial vendors to have some of their modules modified to our specifications. The high-speed readout of a PAD requires that the data be stored at a comparable speed. To satisfy this requirement we need to look at novel techniques to data storage for which we are in consultation with high technology companies to assist us in the design of a high-speed data acquisition system.

Specific Accomplishments: The importance of interacting with experienced CCD designers became immediately clear and resulted in fundamental changes in the design. The most important of these changes are as follows:

1) Device yields will be higher if active structures, such as an amplifier per pixel, are avoided.

2) A MOS CCD-like buried-channel well structure would be able to meet the noise, dynamic range, and timing requirements with higher yields than active structures.

3) A high-Z radiation blocking layer/interconnect structure would have to be microfabricated to separate the radiation sensing pixels from the MOS electronics. This would likely be one of the most challenging parts of the project and will certainly require a microfabrication capability.

4) Yields and the eventual shift to full-size devices would be facilitated by subdividing both radiation sensing and MOS structures, i.e., both sides of the radiation blocking layer would be tiled with smaller chips.

5) A correlated double sampling (CDS) amplifier has been designed and characterized by Sarnoff for military CCD applications. The use of CDS amps allows all eight PAD frames (which may be acquired in < 10 microsec) to be read out within 50 msec, enabling data dumping at video rates. At this data rate, read out is analogue to digital converter (ADC) and storage electronics limited.

After consulting with the electro-optics industry, we were reassured that what we were proposing was feasible. We decided on a plan of action whereby the project was divided into three phases.

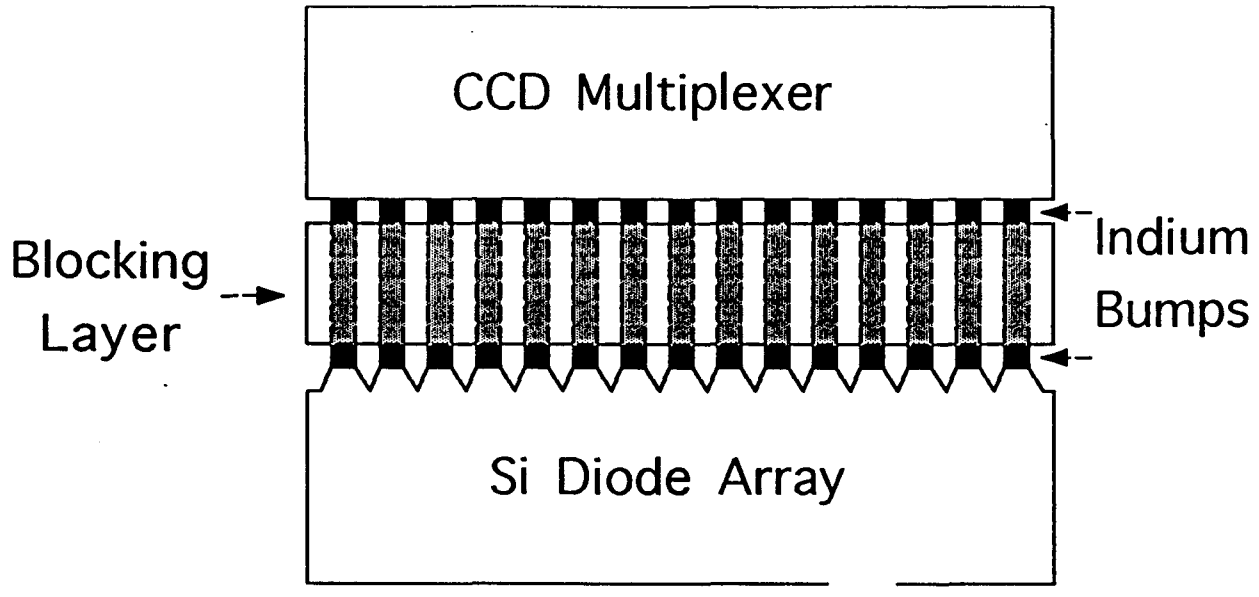
Phase I. Development of 256 x 256 test PADs.
Off-chip electronic design.

Phase II. Scale up to full size PADs.
Assembly of off-chip electronics and software.

Phase III. PAD production and beamline integration.

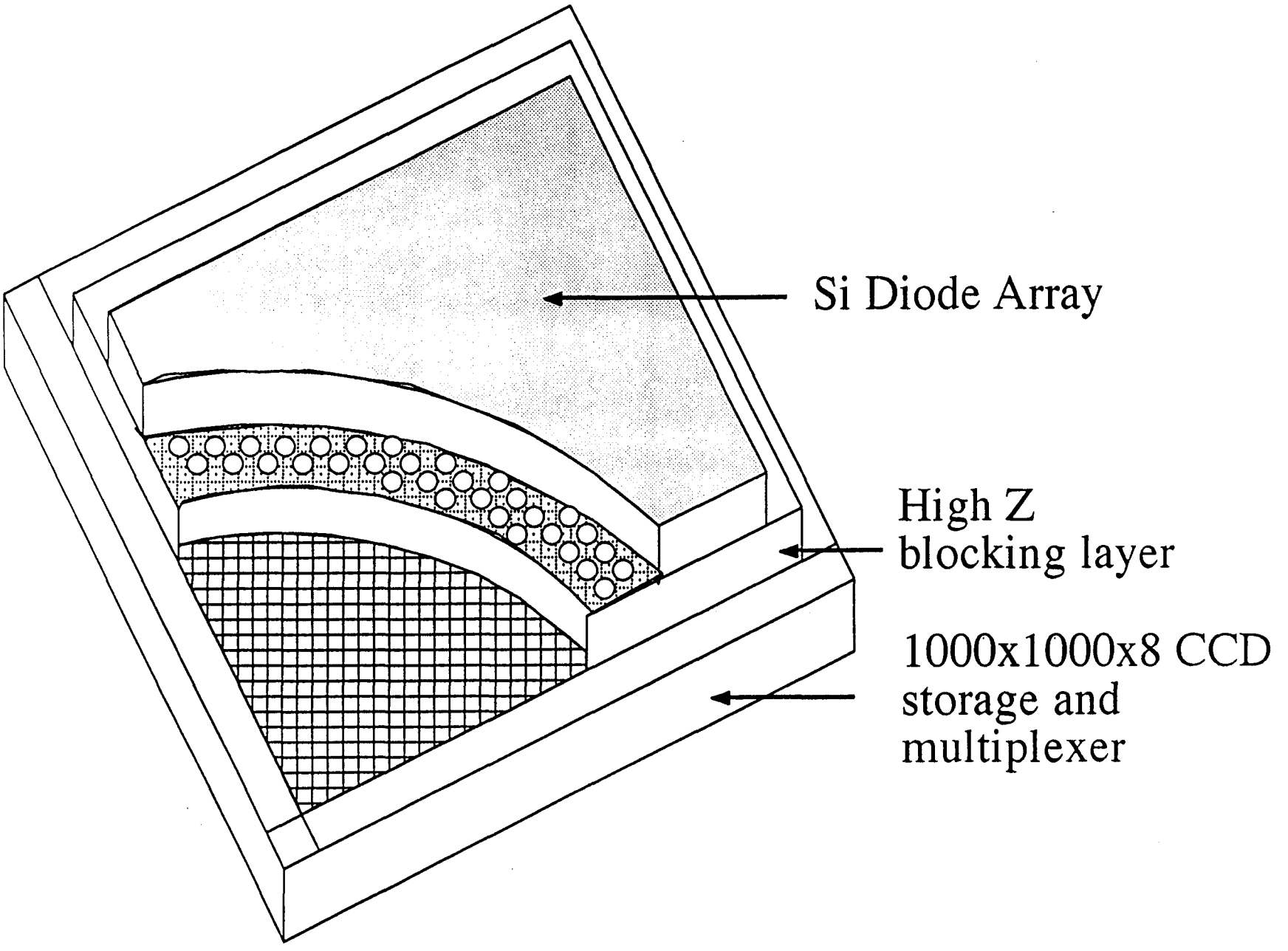
In conclusion, an initial design has evolved having the potential to yield PADs suitable for many of the most demanding imaging applications anticipated at the APS. No other known technology appears likely to meet the needs of microsecond 2-D data acquisition required for time-resolved protein Laue diffraction. A suitable industrial partner has been identified that can offer all the needed design and fabrication facilities. Our suggested strategy is to utilize this resource as the most cost- and time-effective way to realize PADs. This is an opportunity to leapfrog ahead of current detector technology, both in the U.S. and across the globe. The last few months have resulted in the formation of an effective working team capable of implementing PADs and in the generation of the momentum and enthusiasm necessary to make the project succeed.

[1] For a overview, see series *Handbook on Synchrotron Radiation* (North-Holland, Amsterdam, 1983 and 1987).
[2] See "7 GeV Advanced Photon Source: Conceptual Design Report," Argonne National Laboratory Report No. ANL-87-15, April 1987.
[3] B. Rodricks, C. Brizard, Nucl. Instrum. Methods A311, 613-619 (1992).



Hybrid-focal-plane Indium bump bonding

Fig. 1



Hybrid Pixel Array Device

Fig. 2

90-001R2(a) -- DEVELOPMENT OF COHERENT X-RAY FOCUSING OPTICS

Associate Laboratory Director Area: Advanced Photon Source

Principal Investigator: W. Yun, Advanced Photon Source
P.J. Viccaro,* Advanced Photon Source

Funding Profile:

FY 1990†	$389.6K
FY 1991†	$514.1K
FY 1992‡	$196K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: Coherent x-ray microfocusing optics are among the most important optical components that will effectively utilize the high brilliance x-ray beams provided by the third generation synchrotron x-ray sources (e.g., the Advanced Photon Source, European Synchrotron Radiation Facility, and SPring8). The x-ray flux density increases by many orders of magnitude and submicron spatial resolution can be obtained at the focus of such an optical element. These optics can also be used to generate a well-defined x-ray wavefront required in some coherence-based techniques, for example, Fourier transform holography. Combination of these properties with the high brilliance of the third generation sources will open up new opportunities of development of many spatially resolved x-ray techniques, such as microanalysis, microdiffraction, microspectroscopy, and three-dimensional holographic imaging. The development of these techniques will significantly improve our ability to study the spatial distribution of trace elements, crystallographic structures, chemical states, and electronic properties in many material systems. For example, trace element analysis of a sample with submicron spatial resolution and femtogram sensitivity will be possible.

Approach: We analyzed three types of microfocusing optics that have been developed for hard x-ray microfocusing applications and concluded that a Fresnel zone plate is the best candidate as a coherent focusing optic. We analyzed the technical capabilities and the limitations of a sputtered/sliced method and a lithographic method. Both are being developed to produce diffraction-limited phase zone plates for 1-30 KeV x-rays. Based on this analysis, a plan for the production of zone plates using the two methods was established. For x-rays of energies greater than about 10 KeV, the sputtered/sliced method was used in collaboration with Dr. R.M. Bionta of Lawrence Livermore National Laboratory. For x-rays of energies less than 15 KeV, a lithographic method was used in collaboration with Prof. F. Cerrina of the University of Wisconsin at Madison. Several zone plates were produced, and their performance was

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* Currently at CARS, University of Chicago

† Under LDRD "Development of Coherent X-ray Focusing Optics," FY90 - P# 90-001, FY91 - P# 91-049 (90-001R1).

‡ Split off as separate LDRD.

characterized experimentally using synchrotron radiation. The experimental results were analyzed to determine the geometric parameters of the zone plates. These parameters were used in turn to improve the zone plate fabrication process.

Technical Progress and Results: Fiscal year 1990 was devoted mainly to the analysis of the optical requirements of coherent x-ray microfocusing optics and to the development plan of the program. In fiscal year 1991, several prototype Fresnel zone plates were produced and characterized experimentally. Preliminary demonstrations of microfocusing-based techniques, such as microimaging, microanalysis, and microspectroscopy were also made.

In fiscal year 1992, significant advances were made in both the zone plate production and the microfocusing-based x-ray techniques. A Fresnel zone plate with an unprecedented focusing efficiency of 33% for 8 KeV x-rays was experimentally demonstrated. A focal spot size of 0.65 mm FWHM was also obtained from the same zone plate (see figure 1). The measured focal spot size was very close to the diffraction-limited focal spot size of 0.6 mm, which is expected when the zones in the zone plate are well placed and the zone plate is coherently illuminated. Our results indicate that high performance coherent x-ray focusing optics can be obtained.

Several microfocusing-based techniques using the zone plate as a focusing element were also developed. These techniques include microdiffraction, microspectroscopy, microimaging, and microanalysis. Significant information that was not previously available was obtained. For example, using our microprobe, we mapped the distribution of ~1 mm AgBr crystallites on a film as a function of their of crystallographic orientations.

Specific Accomplishments: An Argonne pacesetter award was given for the work on this proposal, and the following publications were produced.

1. "Hard X-ray Phase Zone Plate Fabricated by Lithographic Techniques," B. Lai, W.B. Yun, D. Legnini, Y. Xiao, J. Chrzas, P.J. Viccaro, V. White, D. Denton, F. Cerrina, E. DiFabrizio, L. Grella, and M. Baciocchi,*Appl. Phys. Lett.* **61**, 1877 (1992).

2. "Coherent Hard X-Ray Focusing Optics and Applications," W. Yun, P. J. Viccaro, J. Chrzas, and B. Lai, *Rev. Sci. Instrum.* **63**, 582 (1992).

3. "Mossbauer-Fresnel Zone Plate," T. M. Mooney, E. E. Alp, W. Yun, *J. Appl. Phys.* **71**, 5709 (1992).

4. "Experimental Characterization of Fresnel Zone Plate for Hard X-Ray Applications," B. Lai, J. Chrzas, W. Yun, D. Legnini, and P. J. Viccaro, *SPIE Proc.* **1550**, 46 (1992).

5. "Hard X-ray Microfocusing Techniques Based on Phase Zone Plates," B. Lai, W. Yun, D. Legnini, Y. H. Xiao, J. Chrzas, SPIE International Symposium on Optical Applied Science and Engineering (San Diego, July, 1991).

6. "Hard X-ray Microfocusing Techniques Based on Phase Zone Plates," W. Yun, B. Lai, D. Legnini, Y. H. Xiao, J. Chrzas, K. M. Skullina, R. M. Bionta, V. White, F. Cerrina, SPIE International Symposium on Optical Applied Science and Engineering (San Diego, July, 1991).

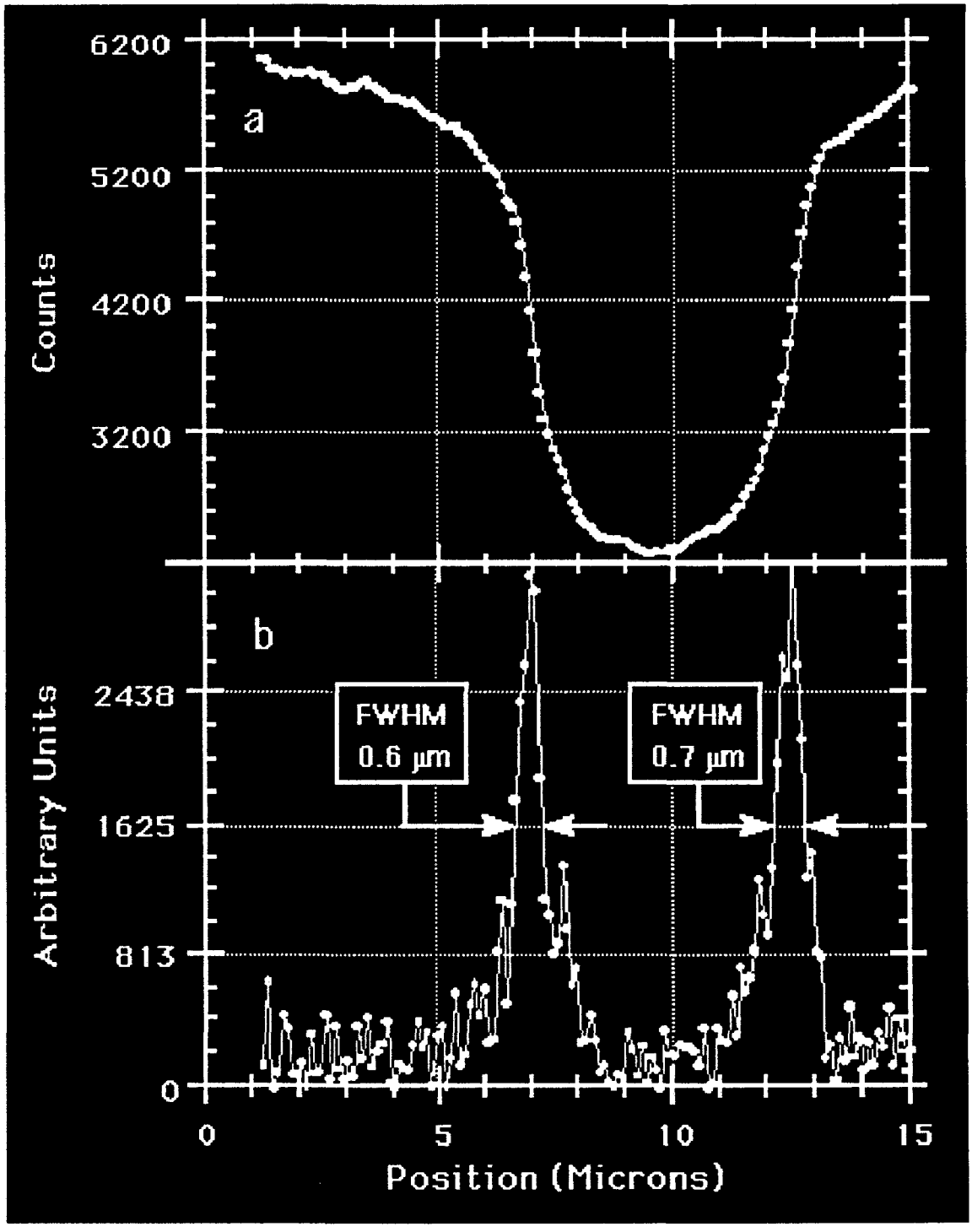

Figure 1. (a) Transmitted intensity measured as a 6-mm-wide Au grid bar was scanned across the primary focus of a Ni zone plate. (b) Absolute derivative of the intensity with respect to the bar position.

92-166 -- HIGH TEMPERATURE SUPERCONDUCTING ELECTRON BEAM LENSES AND WIGGLERS

Associate Laboratory Director Area: Advanced Photon Source

Principal Investigator: J. R. Hull, Materials and Components Technology

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$ 72.5K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: The use of high-temperature superconductors (HTSs) as high-performance electron beam lenses and as wigglers for synchrotron radiation sources and free-electron lasers was explored. The purpose of this project was to determine if HTS electron-beam focussing lenses and wigglers are technically viable with present HTSs, especially as applied to high-energy, relativistic positron beams such as those in the APS, and to develop the theory of diamagnetic electron-beam lenses to determine the physical limits of devices using these concepts.

Approach: Analytical calculations were performed on the basic behavior and phenomena associated with HTS electron beam manipulators using the diamagnetic properties of superconductors. A methodology to determine the behavior of an electron beam interacting with a diamagnetic material was explored both numerically and analytically.

Technical Progress and Results: In general HTS undulators seem feasible and compatible with most requirements of synchrotrons. In particular they may be most appropriate for low wavelength undulators. The phenomena associated with the behavior of HTS undulators have significant differences with those of conventional undulators composed of permanent magnets. The essential difference is that the wavelength tuning depends on the current in the beam. For some machines, this has the potential to yield higher energy photons than with permanent magnet devices. Tuning of HTS undulators will involve different mechanisms than with conventional undulators.

Based on literature values of HTS time response, to first order the HTS can be assumed to respond instantaneously to the beam. This rapid response is responsible for the enhanced focussing effect of HTSs over electrostatic copper lenses. The wake field effects should be no more severe than for conventional beam cavities.

The magnetic field produced by the positron (or electron) beam illicits a response in the HTS. The resulting magnetic field in the HTS then acts on the beam to produce the undulations. Because the field in the HTS depends on the beam, the calculation of detailed beam dynamics is significantly more difficult than for conventional undulators. While several calculational

methods have been developed and a number of calculations have been performed in FY92,

the validity of of these calculations is uncertain because of the lack of experimental data for HTS undulators. Such experiments are recommended for future work.

Specific Accomplishments: Several technical memos were written describing the results of the analytical calculations. These memos and results of this study have been communicated to Jim Vicarro, Efim Gluskin and Roland Savoy of the APS division. A technical journal article summarizing the major findings is in preparation.

90-015R2 -- ATOMIC PHYSICS WITH SYNCHROTRON RADIATION

Associate Laboratory Director Area: Physical Research

Principal Investigator:
P. L. Cowan, Physics
H. G. Berry, Physics
D. S. Gemmell, Physics
Y. Azuma, Physics

Funding History:

FY 1990	$156.3K
FY 1991	$187.5K
FY 1992	$351.3K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: To develop and refine techniques for applying synchrotron radiation, especially x-rays, to studies of atomic physics.

Approach: In anticipation of high-energy x-rays from the Advanced Photon Source (APS) when it comes on line in 3 years time, we are extending our experimental studies of synchrotron radiation-based atomic physics at existing facilities. Specifically, the work is in two parts: (1) new measurements at the X-24A beamline at the National Synchrotron Light Source (NSLS), and at other synchrotron-radiation facilities; and (2) planning and design activities connected with the Basic Energy Sciences Synchrotron Radiation Center (BESSRC) at the APS.

Technical Progress and Results:

Double ionization of helium at high photon energies

In a 1991 collaboration with the University of Tennessee and NIST, we measured the ratio of double to single photoionization of helium at 2.8 keV. During 1992 we extended these results in two sets of measurements (a) at the X-24A NSLS beamline for several well defined photon energies between 2 and 4 keV, and (b) at NSLS beamline X-26 using wide-band-pass radiation with photon energy up to 12 keV. The results confirm most predictions that the ratio approaches a constant at high energy. Our measurements lead to a value of 1.6 ± 0.1 percent, which distinguishes between several different theoretical values.

Photoion charge state yield measurement near Ar-*K* threshold

The charge state yield following K-shell photoexcitation, in the vicinity of the edge region was measured at the NSLS X-24A beamline, utilizing a new time-of-flight (TOF) analyzer constructed by T. LeBrun. The dependence of charge-state distribution on incident photon energy reveals the effect of shake-off and post-collision interaction (PCI). The development of the TOF analyzer has continued and a detector response of 200 psec was achieved.

Fluorescence yield measurement near Ar-*K* threshold

The fluorescence yield of the Ar Kα and Kβ lines were measured with a Si(Li) detector, to address questions concerning PCI raised by the ion yield studies. By measuring the contribution to absorption due to fluorescence relaxation pathways, we were able to isolate the behavior of the dynamic screening versus that of PCI.

Photon-photoion coincidence measurements

Photon-ion coincidence measurements combining the TOF analyzer and Si(Li) detector were done for the first time, in an effort toward more complete measurement of the PCI effect in the near-threshold region.

Ar-*K* Auger satellite and photoelectron satellite measurements

High-resolution electron spectrometry utilizing a cylindrical mirror analyzer was pursued at the NSLS X-24A beamline, in collaboration with the NIST group. Satellite lines of the Auger electrons and photoelectrons due to shake-off and shake-up were measured. Also, data on line-shape distortion due to PCI was obtained.

Resonant Auger Raman measurement

The Auger resonant Raman effect on Ar was studied by measuring the K-$L_2L_3(^1D_2)$ Auger diagram line as well as its 4p and 5p spectator satellites with the Cylindrical Mirror Analyzer (CMA). The incident photon energy was scanned across the resonant excitations and the near K-threshold region. The linear dispersion as well as the narrowing of 4p and 5p spectator satellites characteristic of the resonant Raman effect were observed. The diagram line showed a more complicated structure due to the additional effect from PCI.

Resonant x-ray Raman scattering

The anticipated availability of high-brilliance x-ray sources such as the APS have led to an enhanced interest in high energy-resolution x-ray spectroscopy methods based on x-ray Raman scattering. A study of x-ray Raman scattering near the Xe L-edges was initiated in collaboration with NIST. Preliminary results have provided a convincing demonstration of the importance of multiplet structure in the final state.

Inner-shell double photoexcitation

Our previous measurements of Kr deep-inner-shell double photoexcitation at the Stanford Synchrotron Radiation Lab (SSRL) in collaboration with the University of Oregon group was partially successful, but left a number of open questions. This year we have initiated a series of independent measurements at the NSLS X-24A beamline, utilizing a new set of double ion chambers. Preliminary absorption spectra of Ar show the KM and KL [1s2p] double-

photoexcitation features with improved S/N ratio compared with previous data. The goal is the observation of relativistic and QED corrections to the fine structure of these inner-shell electrons. Also, absorption measurements on alkali-metals utilizing a heat pipe are planned.

Angle-resolved photoelectron spectrometry of atomic nitrogen

Collaborative experiments with C.D. Caldwell of the Univ. of Central Florida and M.O. Krause of ORNL were carried out at the Synchrotron Radiation Center (SRC) in Stoughton, Wisconsin. Angle resolved photoelectron spectrometry of open-shell atoms produced by the dissociation of molecules by microwave discharge was pursued. In particular, the photoionization cross section of atomic nitrogen $2s2p^3$ np autoionizing states and the β parameter over the 2s - 3p and 4p resonances were measured and found to compare favorably with multi-configuration Hartree-Fock (MCHF) calculations.

Photoion charge state yield measurements of alkali metals

The construction of a TOF spectrometer with an oven source to study alkali metals was started. Of particular interest is the double-photoionization measurement of Li by comparing the ratio Li^{++}/Li^{+}. Also, the possibility of studying C_{60} with this apparatus is under consideration.

Planning activities for the BESSRC

Several members of the group have continued to play an active role in the planning for the BESSRC APS beamlines. Specifically, P.L. Cowan has helped in the development of new undulator geometries to improve the medium energy range use. P.L. Cowan has also been working with APS Experimental Facilities Division on x-ray optical problems, and has been invited to participate in the Synchrotron-Radiation Instrumentation CAT.

Conferences attended/invited talks.

Group members attended and contributed to the following conferences: SPring8 Workshop on Atomic Physics, at Himeji, Japan, Mar 23-26, 1992 (Y. Azuma, P.L. Cowan) VUV-X conference in Paris, July 26-31, 1992 (H.G. Berry and T.LeBrun) International Conference on Anomolous Scattering, in Malente/Hamburg, Aug 17-22, 1992 (P.L. Cowan).

Publications

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J. C. Woicik, T. Kendelewicz, K. E. Miyano, P. L. Cowan, M. Richter, B. A. Karlin, C. E. Bouldin, P. Pianetta and W. E. Spicer, "Extended X-ray Absorption Fine-Structure and X-ray Standing Wave Study of the Clean InP(110) Surface Relaxation," J. Vac. Sci. Technol. A **10** (1992) 2041-2045.

S. H. Southworth and P. L. Cowan, "X-ray beam position monitor using a quadrant PIN diode." Nucl. Instrum. and Meth. A **319** (1992) 51-55.

A. T. Macrander, D. R. Haeffner and P. L. Cowan, "Emittance, brilliance and bandpass issues related to an inclined crystal monochromator," SPIE submitted (1992).

91-002R1 -- X-RAY STANDING WAVE STUDIES OF SURFACES AND THIN FILMS

Associate Laboratory Director Area: Physical Research

Principal Investigators: K. Huang, Materials Science
M. J. Bedzyk, Materials Science

Funding History:

FY 1990	$ 0K*
FY 1991	$211.2K
FY 1992	$210.0K
FY 1993	$160K
FY 1994	$ 0K

Purpose: To study the structure of the transition metal silicide/silicon interface during the initial submonolayer and monolayer growth stage. To study the structure and thermal stability of ultrathin organic films deposited on solid substrates. We will develop X-ray synchrotron radiation methods that make use of x-ray standing waves for studying surface, interface and thin film structures. These x-ray interferometry methods when employed at the APS will allow detailed structural information with significantly higher spatial and temporal resolution than presently available.

Approach: Several important phenomena such as total external reflection and the formation of x-ray standing waves and evanescent waves are a consequence of x-rays reflecting from flat surfaces at glancing angles of incidence. We are investigating how these phenomena, which can be described within the framework of Fresnel theory, can be used to study thin film overlayer structures on solid substrate surfaces. In the past, this line of research has led to the discovery of how x-ray standing waves can be used to map out the density profile of ions which are incorporated in the diffuse double layer at the electrolyte / electrode interface [1]. We have also been able to show how angstrom wavelength x-rays can be used to generate x-ray standing waves with very long periods (100 to 1000 Å) to study thin film overlayer structures ranging in thickness from 50 to 1000 Å [2,3].

In our studies we use both the reflectivity and the E-field intensity to study the structure of the overlayer film. The E-field intensity, which is characterized by a standing wave above the reflecting surface and an evanescent wave below the reflecting surface, is sensed by way of the photoelectric effect. The photoeffect in turn gives rise to characteristic fluorescences signals from specific atom types within the thin film. Varying the angle of incidence in the vicinity of the critical angle drastically alters the z dependence of the E-field intensity. Thus as the incident angle is scanned through the reflection, the fluorescence yield from a specific atom spicies modulates in a way which characterizes its density profile in the z direction.

[1] M. J. Bedzyk, G. M. Bommarito, M. Caffrey, and T. L. Penner, Science **248**, 52 (1990).
[2] M. J. Bedzyk, G. M. Bommarito, and J. S. Schildkraut, Phys. Rev. Lett. **62**, 1376 (1989).
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* Although formally included as a subtask of another project in 1990, virtually no attention could be given to this project during that year.

Technical Progress and Results: Most recently, we have investigated a resonanant cavity condition which can be excited in a low density thin film overlayer on a high density x-ray mirror. This resonance condition is brought about by the x-ray beam being "trapped" in the thin film by multiple reflections between the air/film and film/mirror interfaces. The multiple reflections lead to an enhanced x-ray standing wave intensity inside the film with nodes at both interfaces and a first order antinode in the center of the film which is much greater than that produced by two interfering plane-waves.

The thin film for this investigation consisted of a Langmuir-Blodgett (LB) multilayer roughly 1000 Å thick deposited on a gold x-ray mirror surface. The resonance cavity condition, which occurs in the vicinity of the critical angle of the low-density film, is observed in two ways. The first, which is an indirect observation of the resonance, can be seen as a sharp drop in reflectivity. This antireflectant film condition corresponds to the reflected plane waves which reach the detector from the two interfaces being comparable in amplitude, but opposite in phase. The second method of observing this resonance is to directly measure the E-field intensity in the center of the film. This direct observation of the resonace was observed by monitoring the fluorescence yield from a Zn atom layer which had been strategically placed at the center of the film in the LB deposition process. This was the first direct observation of this effect and was made at the Cornell High Energy Synchrotron Source. The results will appear as a report in *Science*.

Future research efforts into the use of this new resonance condition will center around the fact that this effect is very sensitive to film thickness and placement of the atom layer within the film. We will also make use of the E-field intensity enhancement for improving the sensitivity of x-ray scattering and fluorescence from low density monolayers.

Specific Accomplishments:

Publications in press:
"Resonance Enhanced X-rays in Thin Films: A Structure Probe for Membranes and Surface Layers", J. Wang, M.J. Bedzyk, and M. Caffrey, Accepted for publication in Science (1992).
"X-ray Standing Waves at Grazing Angles", T. Jach and M. J. Bedzyk, Accepted by Acta. Cryst. (1992)

Internal Reports:
"X-ray Standing Wave Studies of Submonolayer Gallium Adsorbed on the Silicon (001) Surface", M. J. Bedzyk, Y. Qian, G. E. Franklin, and J. R. Patel, National Synchrotron Light Source 1992 Annual Report.

Conference Presentation:
"X-ray Standing Wave Studies of Ultrathin Films and the Liquid /Solid Interface", M. J. Bedzyk, Invited presentation at the American Chemical Society Conference at San Francisco , April 1992
"X-ray Standing Wave Studies of Surfaces, Interfaces and Thin Films", M. J. Bedzyk, Materials Research Society Conference at Boston , December 1991

92-003 -- NEW TECHNIQUE FOR X-RAY POWDER DIFFRACTION MEASUREMENTS.

Associate Laboratory Director Area: Physical Research

Principal Investigators: M. A. Beno, Materials Science
G. S. Knapp, Materials Science

Funding History:

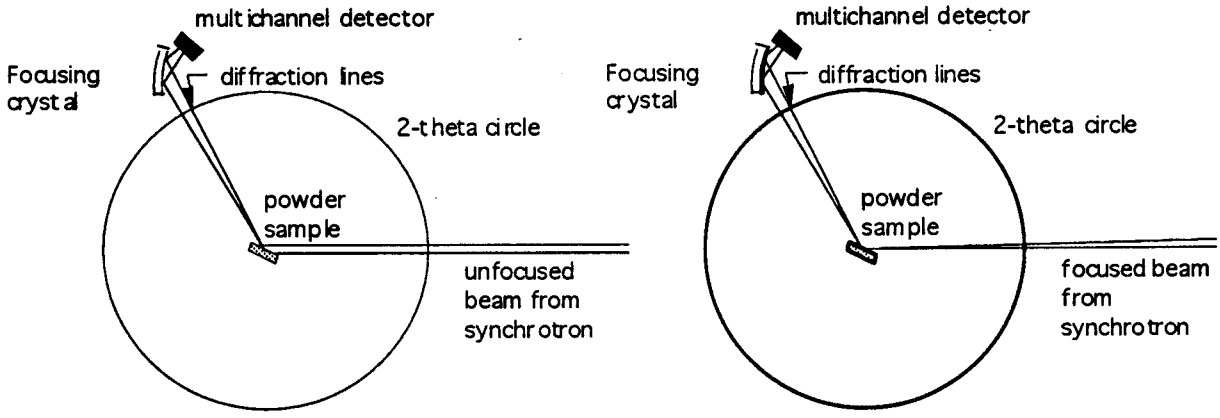
FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$188.1K
FY 1993	$150K
FY 1994	$150K

Purpose: To develop a new technique for rapid acquisition of x-ray powder diffraction patterns. Our emphasis in these investigations is the extension of this technique to the methodology for collection of powder diffraction data at synchrotron sources in short times. This method when employed at the APS will allow detailed structural information to be acquired in submilliseconds.

Approach: Powder diffraction is one of the most important and widely used analytical techniques. The technique is valuable not only for studies of crystalline materials but also in studies of amorphous materials, particularly if the phenomena of anomalous scattering can be utilized. In spite of its great utility, most powder diffraction work is done by methods that were developed generations ago. The best single channel diffractometers employ a diffracted beam monochromator with a single element detector . The diffracted beam monochromator eliminates most of the background caused by sample fluorescence and air scatter. This type of instrument possesses high sensitivity. Trace phases as low in concentration as 0.1% have been determined with this method. An alternative technique employs a position sensitive detector that covers a large solid angle. Position sensitive detectors observe a large portion of the diffraction pattern simultaneously and therefore can achieve rapid collections of x-ray powder patterns. However, these detectors do not have energy resolution and therefore can suffer from high backgrounds particularly for materials containing elements which fluoresce. By using a diffracted beam monochromator together with a position sensitive detector we are developing a number of instruments, both laboratory and synchrotron based, that are much more efficient than existing x-ray powder diffractometers. This increase in efficiency should allow data to be taken in submilliseconds at APS.

Technical Progress and Results. In fiscal year 1992 we have been developed a much more efficient laboratory based diffractometer than the instruments currently in use. We have also done some preliminary measurements at NSLS applied the technique to a synchrotron source. The method uses a focusing diffracted beam monochromator in combination with a multichannel detector. This combination allows us to eliminate the background from fluorescence or other scattering and to take data over a range of 3° to 4° instead of one angle at a time thereby providing a large improvement over conventional powder diffraction methods. The left side of

the figure shows this method as applied on an unfocused synchrotron beamline. In preliminary tests at the X6B beamline, mosaic crystal optics provided very high data rates but only with poor resolution. With perfect crystal focusing optics these tests showed that the field of view is effectively limited by the Darwin width of the focusing crystal so that only a small portion of the incoming x-rays are detected. Nevertheless the method works, achieving a reasonable count rate with very high resolution. The right side of the figure shows how the method can be improved using a focused beam from the synchrotron to bring the flux within the field of view of the diffracted beam focusing crystal. With focusing in both the vertical and horizontal directions the count rate should improve by about a factor of 100 with little loss in resolution. We will be installing a focusing mirror at beamline X6B in the near future and will be testing this concept at that time.



Specific Accomplishments: Active discussions with ARCH and a number of manufacturers of x-ray equipment about marketing a laboratory version of this development.

Patent applied for:
"Powder X-ray Diffraction System", M. A. Beno and G. S. Knapp Dec. 18, 1991

Publications
"A New Method for X-ray Powder Diffraction Studies", M. A. Beno, G. S. Knapp, and G. Jennings, *Rev. Sci. Instrunm.* 4134, **63(9)**, 1992.

To be Published:
" Synchrotron and Laboratory Studies Utilizing a New Powder Diffraction Technique" G. S. Knapp, M. A. Beno, G Jennings, M. Engbretson and M. Ramanathan Presented at the 41st Denver X-Ray Conference and to be published in Advances in X-ray Analysis (Plenum Press) Vol. 36

Conference Presentation:
"New Methods for Time Resolved Diffraction Studies: The Rotating Crystal Laue Technique and Structural Studies Using a New Type of Powder Diffractometer", M. A. Beno, G. S. Knapp, G. Jennings, M. Engbretson and M. Ramanathan, Joint American Crystallographic Association Pittsburgh Diffraction, Conference, Pittsburgh, PA, August 9-14, 1992

90-001R2(b) -- PICOSECOND TIME DOMAIN STUDIES USING SYNCHROTRON RADIATION

Associate Laboratory Director Area:	Physical Research	
Principal Investigator:	J. R. Norris, Chemistry L. Chen, Chemistry	
Funding history:	FY 1990	$389.6K[1]
	FY 1991	$295.5K[1]
	FY 1992	$102K
	FY 1993	$ 0K
	FY 1994	$ 0K

Purpose: We intend to demonstrate the feasibility of determining the structures of molecules in their excited states using synchrotron radiation, such as that from the APS. In particular, we wish to measure the structural changes that occur in photoexcited states of molecules using X-ray absorption fine structure spectroscopy (EXAFS).

Approach: A major unresolved question in several fields concerns the extent to which small structural changes in the excited states of molecules can be measured using X-rays. The pulsed X-rays from the APS may allow measurement of excited state structure and dynamics with a time resolution of about 50 picoseconds. We have initiated work that will ultimately utilize the APS for picosecond time-domain structure determination with X-ray absorption spectroscopies, e.g., EXAFS and XANES, and picosecond time-resolved X-ray diffraction spectroscopy.

Our first goal is to establish time-domain X-ray spectroscopy on excited states. This goal has two major aspects:

1) Demonstration that the structural changes in the excited states of molecules can be measured directly by X-ray spectroscopy. This requires us to show that the structural changes are sufficiently large to be measured directly by X-ray techniques. It also requires us to develop methods for creating large populations of excited states without damaging the samples and to make structural measurements of the excited state in the presence of substantial amounts of the ground state.

2) Demonstration that the structural changes that can be measured are relevant to the physical and chemical properties of the molecules.

Technical Progress and Results: Our initial attempts in FY 1990 to measure the structural changes that occur when zinc tetraphenyl porphyrin (ZnTPP) is photoexcited into its triplet state

[1] Part of FY 1990 and FY 1991 supported work that is now part of the LDRD project: "Development of General Purpose X-ray Shutter for APS."

failed due to our inability to create a large steady-state population of excited states. Most chemical compounds absorb light much more strongly than they absorb X-rays. Thus, when a sufficient concentration is used for the X-ray experiments, it is impossible to keep a substantial fraction in the excited state because most of the light is absorbed by molecules at the surface and never reaches the interior of the sample.

In FY 1991, we turned our attention to molecules that had an extremely long excited state lifetime so that we could use long periods of illumination to convert most of the ground state into the excited state and have it remain there. We identified two good candidates: nickel cyclopentadienyl nitrosyl (NiCpNO) and iron 2-methylphenanthroline (FeMP). In both these molecules, light of one color converts the ground state into an unstable excited state with a lifetime of many minutes. Light of a second color (or heat) drives the molecules back to their ground state. This strategy of using extremely long-lived excited states was necessitated because current second-generation synchrotrons lack both the intensity and pulse structure to perform the experiments we ultimately plan: use of a single X-ray bunch to measure structure. When the third-generation synchrotrons such as APS become available, we will require only a single X-ray bunch and we will be able to use an intense laser pulse to saturate the sample and produce a large transient population of excited states. We are prevented from doing this at present because high-powered lasers will not fire at the repetition rates required to create a large excited state population for every X-ray pulse.

In the current FY 1992 we have succeeded in measuring the structures of both the ground and excited states of NiCpNO and FeMP using EXAFS. For both compounds, light was used to convert the ground state to the excited state and later back to the ground state several times over the course of the measurements with complete recovery of the ground state spectrum. This proved that the changes we saw in the EXAFS spectra came from reversible phototransformations and not from damage to the sample. For both compounds, the difference between the ground state and the excited state EXAFS is easily seen even before analysis.

Initial analysis has been completed for the NiCpNO. In the ground state, EXAFS revealed a structure identical to that obtained by others in the gas phase using microwave spectroscopy. One important feature is that the Ni-N-O atoms lie in a straight line. In the EXAFS spectrum, this linear arrangement produces enhanced scattering signals and a characteristic phase shift from the O atom. In the excited state, the major structural changes were an increase in the Ni-N bond length of about 0.12 Å and a bend of the Ni-N-O bond from linear by 20-30 degrees. These structural changes produced large changes in the EXAFS spectrum because the non-linear arrangement decreased the scattering from the O atom and altered its phase.

The structure of the excited state of the NiCpNO is chemically relevant in two ways. First, the excited state appears to be an intermediate on the pathway used for production of NiCpNO isotopically substituted in the NO group. Second, the excited state is produced by the transfer of an electron from the Ni to the NO group. This excited state is therefore prototypical of excited charge-transfer states that play a central role in photosynthesis and many proposed artificial photoconversion systems.

The FeMP molecule undergoes a high-spin to low-spin transition that can be driven in either direction by light. Nevertheless, these changes in spin produce subtle structural changes that are detected by EXAFS.

Specific Accomplishments: The ground state structure of NiCpNO in condensed phases has been measured by EXAFS and a paper describing it has been accepted for publication by Chemical Physics Letters. The photoexcited state of NiCpNO has been measured by EXAFS and was found to be different from the ground state. This work is currently being prepared for publication and has been presented as posters at two meetings and as a seminar.

The EXAFS spectra of FeMP in its ground and excited states have been measured. There is a noticeable, reversible change in the EXAFS spectrum in going between the two states.

We have demonstrated that structural changes can be measured in excited states of molecules using synchrotron radiation. For NiCpNO, the structural changes occur in a state that is relevant to a chemical substitution process and to electron transfer and photochemical conversion processes.

Publications Include:

"X-ray Absorption Structural Study of a Photoexcited Charge Transfer State", Chen, L. X., Bowman, M. K., Thurnauer, M. C., Montano, P., and Norris, J. R., in preparation

"Molecular Structure of Nickelcyclopentadienylnitrosyl in Condensed Phases Studied by EXAFS, Chen, L. X., Bowman, M. K., Thurnauer, M. C., Lytle, F. W., and Norris, J. R., Chemical Physics Letters, in press.

"Molecular Structure of Nickelcyclopentadienylnitrosyl in Condensed Phases Studied by EXAFS", Chen, L. X., Bowman, M. K., Thurnauer, M. C., Lytle, F. W., and Norris, J. R., Poster, 16th DOE Solar Photochemistry Research Conference, Lake Lawn Lodge, Delavan, Wisconsin, May 31-June 4, 1992

"EXAFS Studies of Molecular Structures for Ground State and Photoinduced Charge Separated State of Nickelcyclopentadienylnitrosyl", Chen, L. X., Bowman, M. K., Thurnauer, M. C., Lytle, F. W., Montano, P., and Norris, J. R., Poster, 9th Intl. Conf. on Photochemical Conversion and Storage of Solar Energy, Beijing, China, August 23-28, 1992

"EXAFS Studies of Photoexcited NiCpNO", Chen, L. X., Seminar, Brookhaven National Laboratory, October 2, 1992

92-110 -- EXPLORATORY INVESTIGATION OF THE APPLICATION OF APS SYNCHROTRON RADIATION TO MEDICAL IMAGING RESEARCH AND TECHNOLOGY

Associate Laboratory Director Area: Energy, Environmental, and Biological Research

Principal Investigator: E.N. Westbrook, Biological and Medical Research

Funding History:

FY 1990	$ 0K†
FY 1991	$ 0K†
FY 1992	$ 47.5K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: To explore the development of a sector of the APS to enable synchrotron radiation to be applied for medical imaging applications.

Approach: In the U.S., direct experience with synchrotron radiation for medical imaging applications has been limited primarily to research conducted at Stanford University's SSRL and Brookhaven National Laboratory's NSLS. By building upon the experience of these groups, plans for the development of a medical imaging research program at the ANL/APS have now advanced through several stages. To date we have studied:

THE CONFIGURATION OF THE APS BEAMLINES, to explore medical imaging interests, needs, and requirements, and alternative configuration approaches to meet them; and

THE FUTURE OF BIOMEDICAL IMAGING MODALITIES, to anticipate developments that experts expect to occur during the next decade in magnetic resonance and spectroscopic imaging (MRI/MRS), computed tomography (CT), radionuclide imaging, ultrasound, and various forms of microscopy.

Technical Progress and Results: Our investigations to date have enabled us to define more clearly the important and unique contributions that synchrotron radiation can make to biomedical imaging research in future decades. The general conclusion drawn from our studies is that x-rays obtainable from the bending magnet (BM) and insertion device (ID) beamlines of the APS are sufficiently intense to form monochromatic beams that are tunable over the range of ~5 to >100 keV. These have the potential for being uniquely advantageous in a variety of important biomedical imaging applications. The research interests of the medical community are focused on the following imaging modes, which appear technically feasible with the APS:

† This study was preliminarily pursued as a minor subtask of larger projects funded in FY 1990 "Biomedical Research Using X-Ray Sources," and FY 1991 "X-Ray Techniques for Biomedical Research."

1) Quantitative X-ray CT. Currently, computed tomography (CT) is performed with a continuous spectrum of x-rays, with the result that the less-energetic x-rays are absorbed more readily. As a consequence, the images reflect penetration of tissue primarily by the more energetic photons. This well-known "beam-hardening" effect results in image artifacts and errors in the measurement of the "stopping power" of tissue. This effect would be eliminated by the use of monochromatic radiation from the APS, and provide a "gold standard" for quantitative x-ray CT imaging. The most challenging technical problem to be addressed is that of devising a means for performing CT rapidly, and hopefully, without rotation of the object (or patient).

2) Dual-energy X-ray CT. Image contrast due to such elements as xenon and calcium, for example, can be enhanced by use of two widely spaced x-ray energies and subtraction of the resultant images. The use of optimized monochromatic photon energies would improve the detection and the measurement of blood flow and perfusion in the brain, using inhaled xenon, and calcium deposits in the breast and vessel walls. Such improvement would contribute to the diagnosis of disorders and diseases of the brain, breast, heart and vessels.

3) Fluorescence Imaging (FI). The use of a scanned beam of monochromatic x-rays just above the absorption-edge of materials with high atomic number (i.e., the so-called high-Z materials), such as iodine and lead, together with a ring of detectors of fluorescence x-rays, would improve the spatial resolution of images and the quantitation of iodine in the thyroid gland and of lead deposits in bone. New adaptations of existing detector and scanning beam technologies would be developed for this application.

4) Coronary Subtraction Angiography (CSA). Interests in the use of monochromatic radiation for CSA emerged in the early 1980s at Stanford University from the collaboration of physicist Robert Hofstadter and physician Edward Rubenstein. The focus of their interest was in solving the technically difficult problem of performing CSA with *intravenously* injected (rather than arterially injected) contrast agents by use of two monochromatic x-ray beams from the SSRL, having energies just above, and just below, the absorption edge of iodine, at 33.17 keV, and by subtracting the resultant images to obtain a single image showing only the iodine. More recently, this research has been continued at Brookhaven's NSLS. Prospects for the development of a successful CSA facility at the APS will be greatly enhanced by building upon the experience of both groups, and by developing new ancillary hardware and software that is beyond the current state of the art. In brief, the feasibility of CSA has been demonstrated; the technical issues that remain include improvement of image quality to compete successfully with alternative diagnostic imaging modalities. In addition, means for performing simultaneous biplane-stereo imaging of the heart to provide some separation of planes in depth, and gated-CT imaging during rotation of the patient are being investigated for this application. Moreover, the possibility exists for the development of new contrast agents with higher Z than iodine, lower viscosity, as well as reduced toxicity and allergic reaction. To this end, pharmaceutical companies are developing new contrast agents.

5) X-ray CT and Holographic Microscopy. These uses of monochromatic radiation to produce 3-D CT images of biological specimens and holographic images of microscopic

structures, such as single cells, are of considerable interest and importance. For x-ray CT imaging of biological specimens, we would build collaboratively upon the experience at NSLS, and for x-ray holographic microscopy, upon the experience at the Lawrence Berkeley Laboratory's ALS, as well as upon the interests and expertise of the ANL Chemistry Division, which has recently embarked on the development of hardware to implement this approach.

6) Radiation Effects. Intense monochromatic photon beams provide the opportunity to study energy-dependent absorbed radiation dose effects, both *in vivo* and *in vitro*. For example, cell preparations treated with various iodine compounds, and exposed to monochromatic radiation just above or just below the absorption edge of iodine would permit the study of the cell-killing effect of such radiation and its enhancement by Auger electrons and very soft fluorescence x-rays that would result from the higher-energy exposure. Extension of these findings to the study of radiation absorbed dose effects *in vivo* may result in important new approaches to radiation therapy, employing both spatial and temporal fractionation of the radiation dose. Such studies would include collaborative research with scientists at NSLS.

Specific Accomplishments: To implement the above studies, some of which present unique and challenging technical requirements, we have investigated development problems associated with potential APS medical applications for the BM and ID beamlines. In particular, it should be noted that applications 1) and 2), and possibly 3) and 4), will require spreading the beam width to approximately 50 cm, which will require extension of one or both beamlines beyond the perimeter of the APS building. Alternative ways of meeting these and other requirements are currently being evaluated.

90-001R2(c) -- DEVELOPMENT OF COHERENT-BASED TECHNIQUES

Associate Laboratory Director Area: Advanced Photon Source

Principal Investigator: W. Yun, Advanced Photon Source
P.J. Viccaro,* Advanced Photon Source
E. Gluskin, Advanced Photon Source

Funding Profile:

FY 1990†	$389.6K
FY 1991†	$514.1K
FY 1992‡	$196K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: The objective of this program was to develop techniques that utilize the unprecedented coherent power of third generation synchrotron sources under construction worldwide, such as the Advanced Photon Source, ESRF, and SPring8. To take full advantage of these techniques, it is essential to study their feasibility, to develop the necessary x-ray optics, and to conduct preliminary experiments to demonstrate the underlying principles.

Approach: X-ray holography, interferometry, and phase-sensitive signal enhancement are coherence-dependent techniques that offer substantial advantages over non-coherence-based methods, which include most of those currently in use. We selected these three techniques to study because of their high potential utility. X-ray holography is promising as an imaging technique capable of sub-optical spatial resolution with phase contrast, lower specimen damage than electron-based microscopy, and flash exposures. In particular, the Fourier transform holography geometry offers spatial resolution that is independent of the detector resolution and is free of the twin-image noise associated with in-line geometry. X-ray interferometric methods are essential for making precision measurements of material optical constants, reflection coefficients, anomalous dispersion, and coherence of x-ray beams. For instance, an x-ray Michelson interferometer capable of scanning over many interference orders would be invaluable for Fourier transform spectroscopy. By contrast, x-ray intensity interferometry promises to be a highly sensitive beam coherence and source diagnostic technique that is immune to the tight optical tolerances inherent to amplitude interferometry. Finally, we considered x-ray signal enhancement techniques that can greatly increase the detectability of a signal wave by selectively enhancing or suppressing some of its components by interference with an appropriately adjusted reference wave.

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* Currently at CARS, University of Chicago.
† Under LDRD "Development of Coherent X-Ray Focusing Optics."
‡ Split off as separate LDRD.

Technical Progress and Results: This R&D program has made significant experimental and theoretical achievements toward realizing these three coherence-based techniques.
Development of x-ray Fourier transform holography has proceeded along two complementary paths. High resolution holography experiments were carried out with coherent soft (0.35 KeV) x-rays and resolution test objects to simulate experiments with higher energy x-rays.[1,2] The high brilliance X1 undulator at the NSLS provided the necessary coherent flux. The results (figure 1) show that a transverse resolution of 60 nm is possible with this technique, which is consistent with diffraction-limited performance of the zone plate optic used. In parallel, we have assessed the feasibility of Fourier transform holographic microscopy using harder (2-4 KeV) x-rays produced by a third generation undulator source. We anticipate that hard x-ray holography with submicron resolution is practical using high efficiency (>30%) phase zone plates, such as those that we have recently developed and tested with 8 KeV x-rays.[3,4] In addition, a large-format, low-noise, liquid-nitrogen-cooled CCD camera was acquired. This detector has the sensitivity and number of pixels (1024 x 1024) needed for wide-aperture x-ray holography.

The second coherence-based technique we have pursued is x-ray intensity interferometry. This work includes a study of the feasibility of coherence measurements of the intense x-ray beams produced by the third generation sources, and the design of a current-mode intensity interferometer to be tested with an existing high brilliance second generation soft x-ray undulator.[5-7] With this instrument, we expect that spatial coherence measurements of high brilliance undulator beams will be possible on time scales of several minutes. The interferometer (figure 2) will be a UHV device consisting of an array of pairs of slits on a two-axis stage, a wedge-shaped beam splitter, two fast microchannel plate detectors with matched preamplifiers, and a low-noise, low-drift correlator circuit.

Lastly, we studied several coherence-based x-ray signal enhancement techniques, and we considered the most efficient phase-shifting materials for 0.1-10 KeV x-rays.[8] As a consequence, several wedge-shaped beryllium blocks were acquired to demonstrate their phase-shifting capabilities with hard x-rays. The blocks could be used in conjunction with an amplitude interferometer to analyze the complex reflection coefficient of a surface or to provide the large phase shift necessary for high resolution Fourier transform spectroscopy.

Specific Accomplishments:

1. "High Resolution Imaging by Fourier Transform X-ray Holography," I. McNulty, J. Kirz, C. Jacobsen, E.H. Anderson, M.R. Howells, and D.P. Kern, *Science* **256**, 2009 (1992).

2. "First Results with a Fourier Transform Holographic Microscope," I. McNulty, J. Kirz, C. Jacobsen, M.R. Howells, and E.H. Anderson, ed. by A.G. Michette, G.R. Morrison, and C.J. Buckley, **X-Ray Microscopy III** (Springer-Verlag, Berlin, 1992) p. 251.

3. "Hard X-ray Phase Zone Plate Fabricated by Lithographic Techniques," B. Lai, W.B. Yun, D. Legnini, Y. Xiao, J. Chrzas, P.J. Viccaro, V. White, D. Denton, F. Cerrina, E. DiFabrizio, L. Grella, and M. Baciocchi,
Appl. Phys. Lett. (October 1992).

4. "Coherent Hard X-ray Focusing Optics and Applications," W.B. Yun, P.J. Viccaro, B. Lai, and J. Chrzas, *Rev. Sci. Instrum.* **63**, 582 (1992).

5. "Intensity Interferometry and its Application to Beam Diagnostics," E. Gluskin, **1991 IEEE Particle Accelerator Conference** (IEEE, New York, 1991) Vol. 2, p. 1169.

6. "X-ray intensity interferometer for undulator radiation," E. Gluskin, I. McNulty, M.R. Howells, and P.J. Viccaro, *Nucl. Instr. Meth.* **A319**, 213 (1992).

7. "Comment on 'Interference Effects Between Independent Gamma Rays'," I. McNulty, E. Gluskin, and M. Howells, submitted to *Phys. Rev. Lett.*.

8. "Phase Shifters for X-rays," W.B. Yun, I. McNulty, and B. Lai, *LS-Note* (Advanced Photon Source, Argonne National Laboratory), in preparation.

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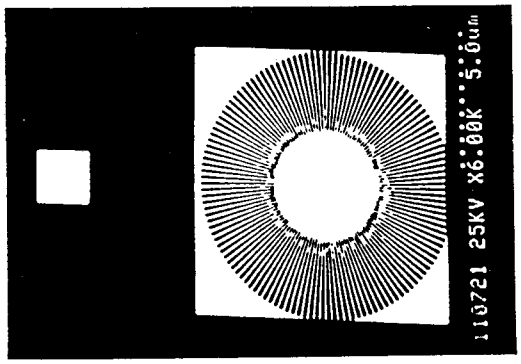

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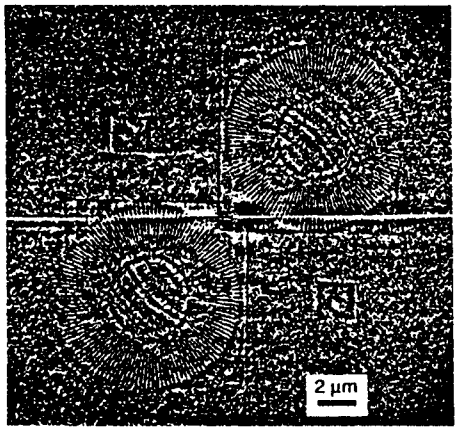


Figure 1. (A) Scanning electron microscope image of a microfabricated gold test pattern. (B) Fourier transform hologram of the test pattern recorded with 3.4 nm x-rays. The exposure time was 10 min. (C) Numerical reconstruction of the hologram. Lines and spaces at the 60 nm scale are clearly visible in the reconstructed image.

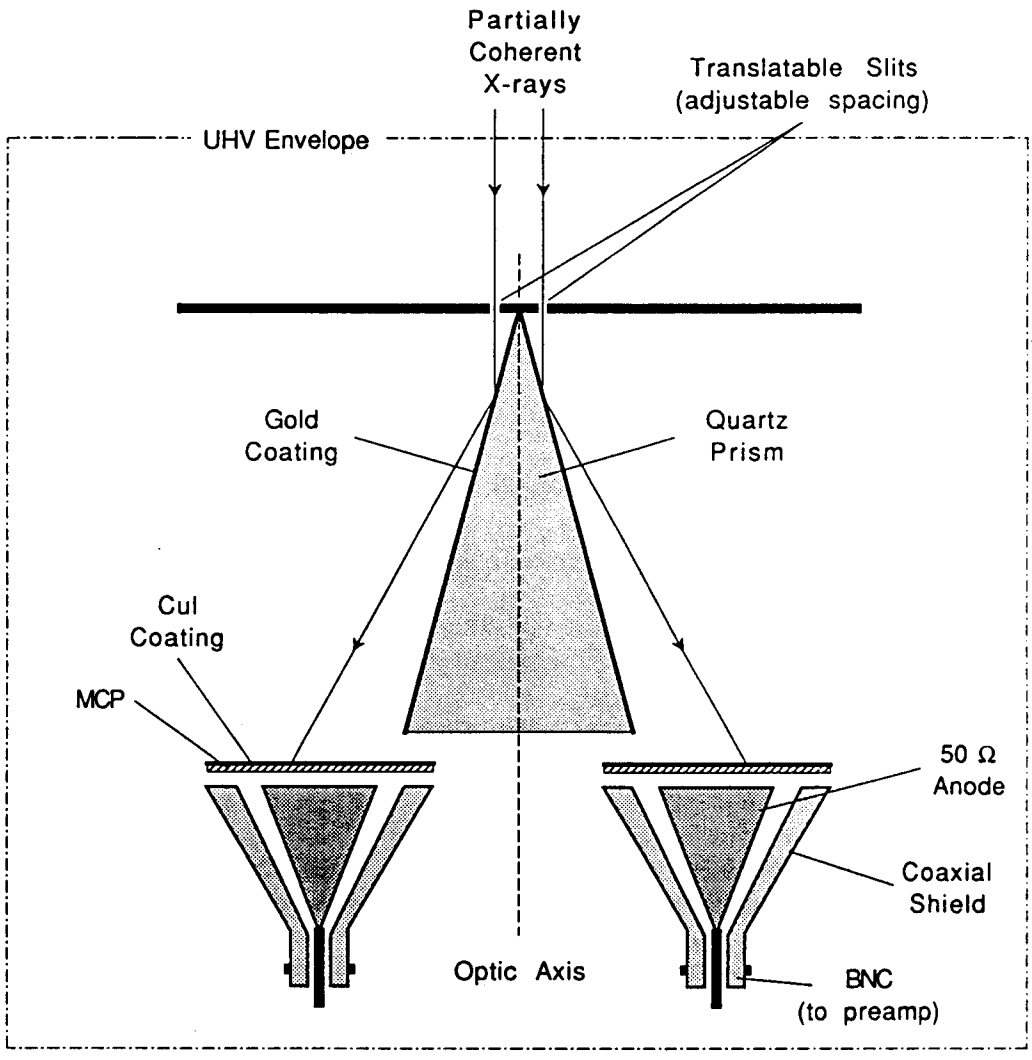


Figure 2. Schematic design for an intensity interferometer for soft x-ray undulator radiation.

91-022R1 -- ADVANCED REACTOR DESIGN STUDIES FOR A 600 MWe LMR BASED ON EBR-II TECHNOLOGY

Associate Laboratory Director Area: Engineering Research

Principal Investigator: R. W. Seidensticker, Reactor Engineering
D. R. Pedersen, Reactor Engineering

Funding Profile:

FY 1990	$ 0K
FY 1991	$306K
FY 1992	$288K
FY 1993	$350K
FY 1994	$ 0K

Purpose: The main purpose of this study is to develop a reference LMR design concept which utilizes those essential features of EBR-II which are believed to have contributed the most to the success of the EBR-II reactor. In particular, the study is intended to demonstrate feasibility of extrapolating these essential features of EBR-II to a larger plant, and to explore any modifications needed in these features to achieve this basic feasibility.

Approach: This study is carried out by a small group of engineers at ANL experienced in LMR plant design, including several members who participated in the original design of EBR-II. The approach used to effect this study consisted of a central effort which focussed on developing conceptual layouts of alternate primary system concepts. These layouts were critically reviewed and discussed by the study team to establish a reasonable baseline, or reference, design concept. A limited amount of hand calculations were made to establish the reasonableness of the system configuration. A study was made to establish the basic features of a steam generating system for a 600 MWe plant based on extrapolating the highly successful double-wall tube design used in EBR-II.

Technical Progress and Results: Technical progress in FY92 included the development of those engineering features of a large (600 MWe) LMR plant which are needed to adapt the EBR-II concept to the larger plant. In particular, the fundamental attribute of EBR-II of a low and constant bulk sodium temperature requires a "closed" pipe connecting the outlet plenum of the reactor to the inlet of the intermediate heat exchanger (IHX). In EBR-II this is accomplished by using a very flexible, Z-shaped, pipe between the reactor outlet and the IHX. In a 600 MWe plant this approach becomes very expensive and may be even impractical due to the large diameter (30-36 inches) pipe loops required. To obtain sufficient flexibility in such large-diameter pipes it is necessary to have a long run of piping (several tens of feet) between the reactor and the IHX. At least three (3) such expansion loops are needed, and the amount of physical space required for these loops result in a primary sodium tank diameter much larger than that required for other LMR concepts (e.g., SuperPhenix).

Thus, the ANL design for the 600 MWe plant uses an articulated, short, stubby pipe which connects directly between the reactor outlet plenum and the IHX. This pipe must operate over a wide range of temperatures, 650°F at cold, standby to 950°F at power operation. The pipe stub must be tight enough to minimize leakage, be loose or flexible enough to accommodate the large thermal movements and be stable enough to avoid flow-induced vibration. In addition it was decided to provide the feature of complete removeability of these short outlet pipes in the extremely unlikely event of any serious malfunction or failure. It is anticipated that this removal capability will be required by a utility owner of any such LMR plant.

Highly reliable decay heat removal systems are crucial to any reactor plant. For any LMR reactor system, and for a pool-type system in particular, it is generally required to use two, independent and diverse decay heat removal concepts. For the current 600 MWe concept, it was decided to use one system of bayonet-type dip-coolers (which are similar to the shutdown coolers used in EBR-II). The second, diverse decay heat removal system used is the placement of cooling coils located at the top of the IHXs. While the latter system results in a somewhat longer IHX, it is quite effective in removing the decay heat because, being located directly in the hot reactor coolant stream, natural circulation is quickly established following any loss of normal pumping power.

Specific Accomplishments: A baseline, or reference conceptual layout was prepared. An exploratory design of the short stub pipe between the reactor outlet plenum and the IHX was effected. This concept was carried out in sufficient detail to show a feasible scheme needed to remove these stub pipes in the very unlikely event of their failure or malfunction.

A layout was prepared of a steam generating system (for the 600 MWe plant) which employs the highly successful double-walled tube design used for EBR-II. This steam generating system was based on a thorough analysis of the details used in the EBR-II concept design and fabrication, with great emphasis on the fabrication aspects of the approach.

The study team made a detailed, one (1) day presentation to a large number of engineers and managers at the EBR-II site in Idaho.

92-041 -- USE OF ION CONDUCTORS IN THE PYROCHEMICAL REDUCTION OF OXIDES

Associate Laboratory Director Area: Engineering Research

Principal Investigators: W. E. Miller, Chemical Technology
V. A. Maroni, Chemical Technology

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$195.3K
FY 1993	$210K
FY 1994	$100K

Purpose: This LDRD project (started in FY 1992) has as its main purpose the development of an electrochemical oxygen pump capable of removing oxide ions (O^{2-}) dissolved in molten process salts that are used in the reduction of transuranic oxides to the metal form. A secondary purpose of the project is to investigate methods of combining the O^{2-} oxidation (to O_2) and the metal oxide reduction steps into a single electrochemical process. If successfully developed, the proposed process could be used to reduce spent oxide fuel and oxidized mixed transuranic waste to the metal form, which could then be fed directly to an Integral Fast Reactor (IFR)-type electrorefiner. A convenient, compact head-end method for coupling a wide range of transuranic wastes to the IFR fuel cycle is starting to emerge from the results of work done in FY 1992. However, even if only the main purpose is achieved, there are still numerous opportunities for indirect coupling of the oxide removal capability with pyrochemical reduction techniques, such as those currently under development in the Actinide Recycle Program.

The development of ion conductors and electrochemical metal oxide reduction processes that utilize them could have wide application not only in the nuclear industry, but also in the metals production industry. This process also holds the promise of being able to clean up waste salts (e.g., produced in the weapons program) that are contaminated with actinide oxides. A potential long-term payoff to such an approach is to make actinide oxide reduction a compact, continuous operation in which transuranic elements are consolidated, purified, and prepared for recycle, without need for temporary or long-term storage.

Approach: The focus of this LDRD project is on developing and testing a rugged oxide-ion-conducting material suitable for use in molten alkali and alkaline earth halide melts at temperatures in the vicinity of 800°C. A number of ceramic materials have high oxide ion conductivities at temperatures in the 750 to 1000°C range. ZrO_2 and ThO_2 stabilized with lower valent cations, e.g., yttrium(III) and calcium(II), are but two examples. Such materials currently find use in oxygen sensors and as fuel cell electrolytes. Recently, there has been an effort on the part of at least one manufacturer (Ceramatec Inc.) to develop these materials as oxygen pumps (e.g., for separation of oxygen from other gases and for oxygen purification)

and as electrolytes for high-current-density electrolytic devices. Our approach is based on the use of such oxygen pumps to draw O^{2-} out of molten salt baths, oxidize the O^{2-} to O_2 in a separate compartment, and sweep the O_2 out of the processing environment. It is highly desirable to have the cathodic reaction accompanying the O_2 evolution be one that produces a useful product.

In brief summary, an oxide-ion-conducting ceramic tube with a closed bottom end is immersed in a molten salt bath together with a noble metal counter electrode. Negative potential is applied to the metal electrode, and positive potential is applied to a current collector lead (e.g., silver) attached to the inside of the ceramic tube using a cermet. If a potential is applied and if oxide ions are present in the melt, the oxide ions will diffuse through the ceramic tube and be oxidized to O_2 along the silver/cermet current collector. By passing an inert sweep gas (e.g., argon or helium) through the inside of the tube, the O_2 can be swept away so that the oxygen potential gradient across the tube wall (the gradient driving the O^{2-} through the wall) can be maintained. To achieve and maintain a high current density, the O^{2-} concentration in the molten salt must remain at near-saturation levels. This can be accomplished by constantly feeding a soluble metal oxide to the salt or introducing an insoluble metal oxide that is reduced by the metal being deposited at the cathode. In the case that is being studied, the salt is a mixed alkali chloride/alkaline earth chloride eutectic, and the cathode deposit is an alkali or alkaline earth metal that will reduce transuranic oxides. The reduced transuranic metal should sink to the bottom of the cell, from whence its recovery is a straightforward matter.

Technical Progress and Results: Major contributions to the laboratory effort were made by two empolyees -- Prof. Samuel von Winbush, a visiting faculty member on sabbatical leave from the State University of New York (Old Westbury Campus), and Mr. Stanley A. Johnson, a Chemist in the Chemical Technology Division. Preliminary tests were conducted with two commercially available, high-temperature, oxide-ion-conducting ceramics -- yttria-stabilized zirconia (YSZ) and calcia-stabilized zirconia (CSZ) -- in $LiCl$-$BaCl_2$-$NaCl$-$CaCl_2$ eutectic containing dissolved CaO. The results gave immediate definitive evidence that electrochemical extraction of O^{2-} from the molten salt could be achieved around 750-800°C, as proposed. However, the highest current densities attained in these preliminary tests were only in the milliampere/cm^2 range. Continued investigation of this first series of YSZ and CSZ tubes revealed that the homemade current collector attachments to the inside of the ceramic tubes were much too resistive. During the course of subsequent inquiries to YSZ and CSZ vendors, it was discovered that Ceramatec, Inc. (Salt Lake City, Utah) was developing YSZ tubes with special high-performance internal current collectors. Several of these tubes were purchased and tested to determine whether they would function in $LiCl$-$BaCl_2$-$CaCl_2$ eutectic. The first experiments were performed in the 750-800°C range using a molybdenum screen as the counter electrode and measured quantities of added CaO as the source of oxide ions. With the specially fabricated YSZ tubes made by Ceramatec, it was possible to obtain current densities near 0.1 A/cm^2 at ~3.5 V. Figure 1 presents sketches of the test loop configuration and the molybdenum current collector/ion conductor embodiment used in these

experiments. Figure 2a shows the results of oxygen evolution tests at temperatures between 750 and 825°C.

A considerably more interesting test employing the proposed combined redox process was performed, in which the counter electrode was a liquid bismuth-tin alloy, and CeO_2 was added to the melt to provide a representative stand-in for UO_2. With this arrangement (see Fig. 1) current densities near 0.15 A/cm^2 (based on the oxygen evolution rate at constant voltage) were measured. The measured total electrical current was typically only 10% higher than the O_2 evolution current, giving evidence of a highly efficient electrochemical cycle. It is important to note here that the CeO_2 does not dissolve in the molten salt eutectic to any great extent but rather reacts with the alkali and alkaline earth metals generated on the surface of the bismuth-tin cathode (during application of voltage) to form cerium metal and soluble alkali and alkaline earth oxides. Thus, the electrodeposited alkali and alkaline earth metals are returned to the salt together with the O^{2-} ion, while the cerium metal dissolves in the liquid bismuth-tin. Oxygen evolution data collected during a set of runs at 775°C with the bismuth-tin cathode are shown in Fig. 2b. The application of this process to UO_2 and transuranic elements is expected to proceed in essentially the same way, although the choice of solvent for the reduced metal may differ.

The emphasis of future work on this project should be in three areas: (1) testing of the existing process methodology on UO_2, (2) further development of the solid electrolyte (e.g., in collaboration with Ceramatec, Inc.) to identify/produce an O^{2-} ion conductor capable of current densities approaching the pilot-scale goal (0.5 A/cm^2), and (3) electrochemical performance tests using cyclic voltammetric and ac impedance methods to determine the rate-limiting step in the coupled redox cycle. There is some evidence that the overall current density levels and current efficiency are limited by the metal oxide reduction reaction. If this proves to be the case, efforts should be made to enhance the rate of the reduction process by incorporating mixing, improved cell designs, and higher temperatures.

Specific Accomplishments: From this work has come a clear definition of the research needs/direction for the ion-conductor-based pyrochemical reduction of oxides in FY 1993. The functional aspects of the process have been demonstrated, including both electrochemical O^{2-} removal from molten salt baths and the coupling of the oxidation and reduction reaction into a single electrochemical cell. Current densities approaching 25% of the goal level (0.5 A/cm^2) for a desirably sized, pilot-scale electrolytic cell have been reached. Solid electrolyte material performance, although at an early and limited stage of selection/development, has been very encouraging. An invention report describing the patentable aspects of the use of ion conductors in the pyrochemical reduction of oxides (ANL-IN-91-74), by W. E. Miller and Z. Tomczuk, has been submitted to DOE.

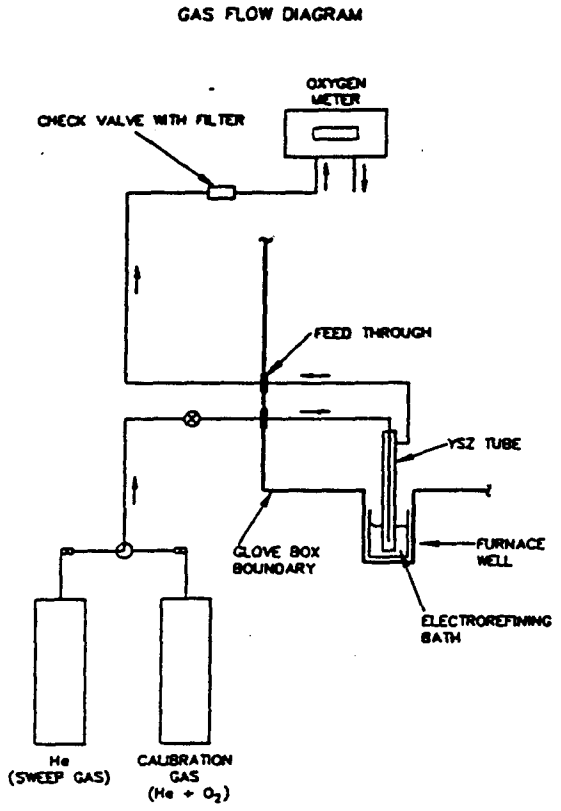
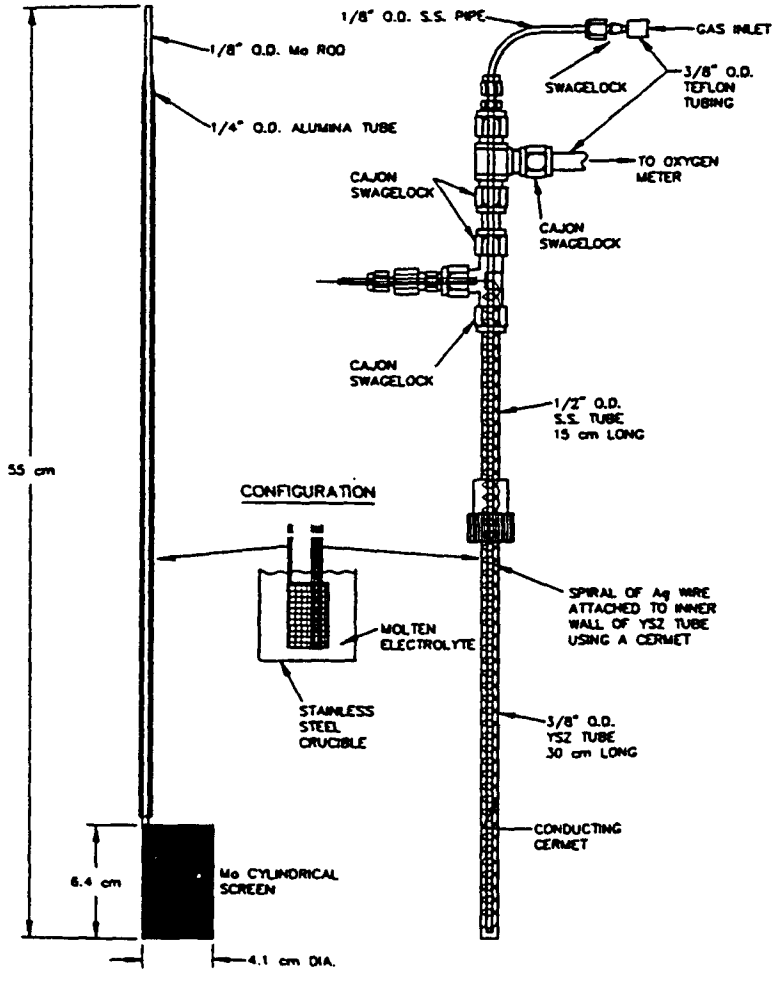
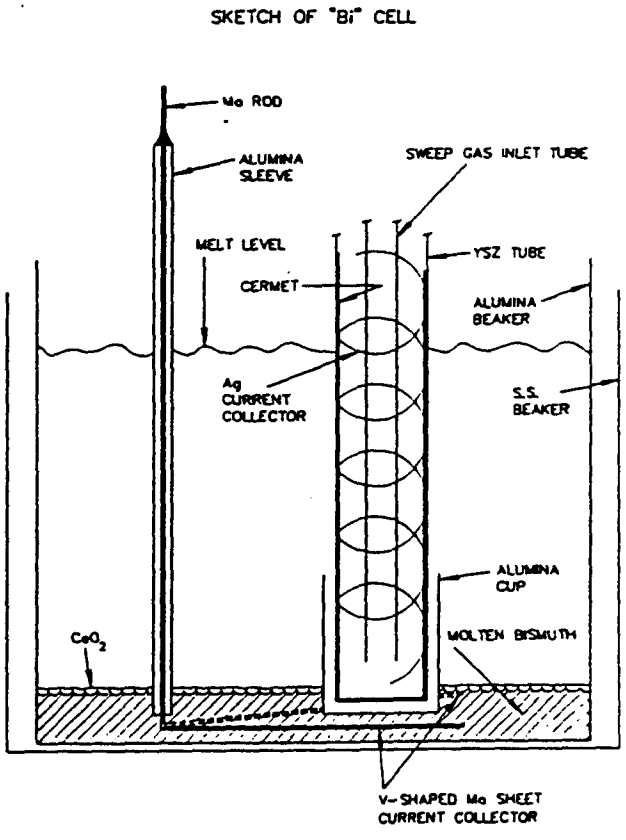


Figure 1. Sketches of the test loop configuration for the ion conductor experiments (upper left), the molybdenum current collector/ion conductor cell embodiment (lower left), and the bismuth-tin/ion conductor cell embodiment (lower right).





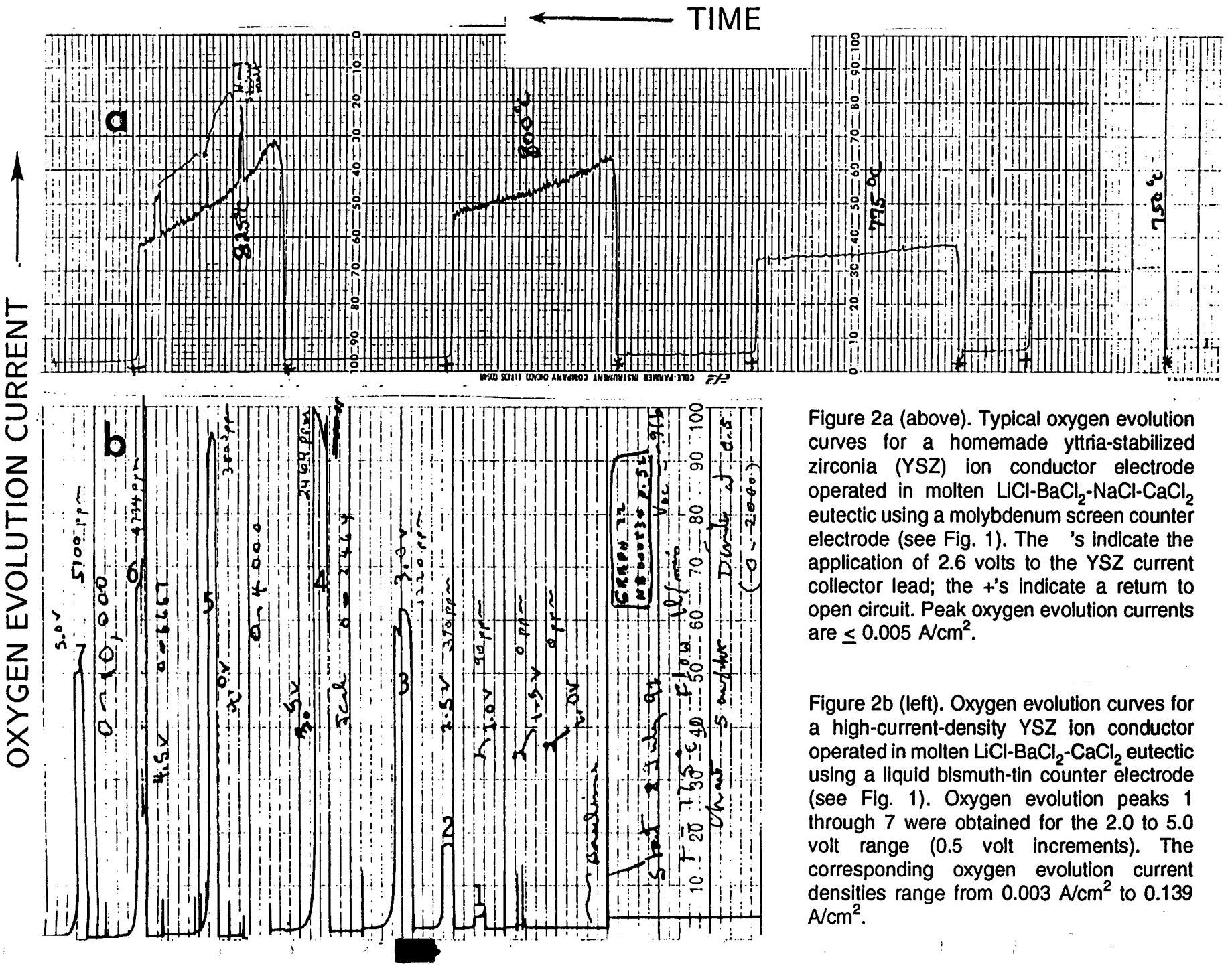


Figure 2a (above). Typical oxygen evolution curves for a homemade yttria-stabilized zirconia (YSZ) ion conductor electrode operated in molten LiCl-$BaCl_2$-NaCl-$CaCl_2$ eutectic using a molybdenum screen counter electrode (see Fig. 1). The 's indicate the application of 2.6 volts to the YSZ current collector lead; the +'s indicate a return to open circuit. Peak oxygen evolution currents are $\leq$ 0.005 A/cm^2.

Figure 2b (left). Oxygen evolution curves for a high-current-density YSZ ion conductor operated in molten LiCl-$BaCl_2$-$CaCl_2$ eutectic using a liquid bismuth-tin counter electrode (see Fig. 1). Oxygen evolution peaks 1 through 7 were obtained for the 2.0 to 5.0 volt range (0.5 volt increments). The corresponding oxygen evolution current densities range from 0.003 A/cm^2 to 0.139 A/cm^2.

92-047 -- COMPUTER IMAGING OF EBR-II FUEL HANDLING EQUIPMENT

Associate Laboratory Director Area: Engineering Research

Principal Investigator: K. J. Allen, Integral Fast Reactor Operations

Funding Profile:

FY 1990	$ 0
FY 1991	$ 0
FY 1992	$ 164.6K
FY 1993	$ 125K
FY 1994	$ 150K

Purpose: This project develops an acoustic imaging technique to provide a computerized three-dimensional real-time display of fuel handling equipment submerged and operated in the EBR-II primary tank liquid sodium. This approach differs from other acoustic imaging efforts by mapping signals to a previously generated computer model instead of by creating images of the actual under-sodium objects. The result of this project will be a method to visually display the positions of critical components and to provide an independent cross-reference of their positions as indicated by the existing position switches and meters. This acoustic imaging will improve the fuel handling surveillance and troubleshooting efforts and may be applicable to other hostile environments in which the positions of critical equipment must be known.

Approach: EBR-II reactor fuel and experiments are transferred into and out of the reactor vessel via remotely operated fuel handling equipment. The radioactively contaminated 700°F liquid sodium environment prevents direct visualization of the subassemblies and fuel handling equipment during these transfers. The position of the fuel handling equipment is now inferred by sensors mounted outside of the hostile environment of the primary tank. Observation of the equipment within the primary tank has not been possible since the initial filling with liquid sodium more than twenty five years ago.

A three-dimensional (3D) computer model of the existing EBR-II fuel handling equipment is being created in an AutoCAD format by C. V. Wiegand from the original two-dimensional blueprints. This model will be used for development of the acoustic equations by mapping the relative locations of equipment that can reflect or distort the active acoustic signals. In addition, the model will become the animated display presented to the operator during fuel handling.

The development of an acoustic sensor echo-location technique was initiated by G. G. Peters and L. H. Hansen to detect the position and relative movement of the fuel handling equipment. Software will subsequently be developed to process the acoustic sensor signal information, correlate it with the 3D computer model, and display an animated image in real-time. A scaled mockup of the primary tank and equipment will be used to test the accuracy

and reproducibility of the technique and software display. Some of the materials needed to support mockup testing are being procured.

After the echo-location technique is determined, the existing acoustic sensors installed in the primary tank will be evaluated for suitability and, if necessary, redesigned to fulfill the echo-location technique requirements. A high temperature sodium-immersible acoustic transmitter and appropriate electronics will be designed and built to provide an active sound source.

After the method and equipment have been shown to perform satisfactorily outside of the reactor, procedures will be written for the installation and testing of the equipment and software in the EBR-II primary tank. Testing during actual fuel handling will be performed and evaluated for effectiveness of the technique and equipment.

Technical Progress and Results:

The AutoCAD model of the primary tank and fuel handling equipment was initiated and is now 80% complete. The attached figures were plotted from this 3D model and show the congested and complex environment in which the acoustic imaging technique will have to work. The display software, SDRC I-DEAS, was installed to allow an animated display of the equipment positions. Conversion of the model from the AutoCAD format to the I-DEAS format was initiated. A Silicon Graphics Crimson computer workstation was installed to perform both the acoustic signal processing and the graphics display tasks.

Literature searches were initiated to correlate other acoustic research efforts with the particular needs of this task and this environment. Other researchers have performed under-sodium acoustic imaging but this project is unique in its approach to mapping the positions of components to a pre-existing electronic model of the imaged items.

The continuation of this effort in FY 1993 is expected to result in the completion of the AutoCAD model and its conversion to the I-DEAS software. Development of the acoustic equations required for the primary tank environment will continue and be tested outside of the reactor in a scaled mockup. The acoustic signal processing requirements will be identified and tested on the workstation. The programming methods and database manipulations required to move the equipment in the I-DEAS display software will be developed and tested on the workstation.

Specific Accomplishments:

This project was initiated in April 1992. Since April, good progress was made.

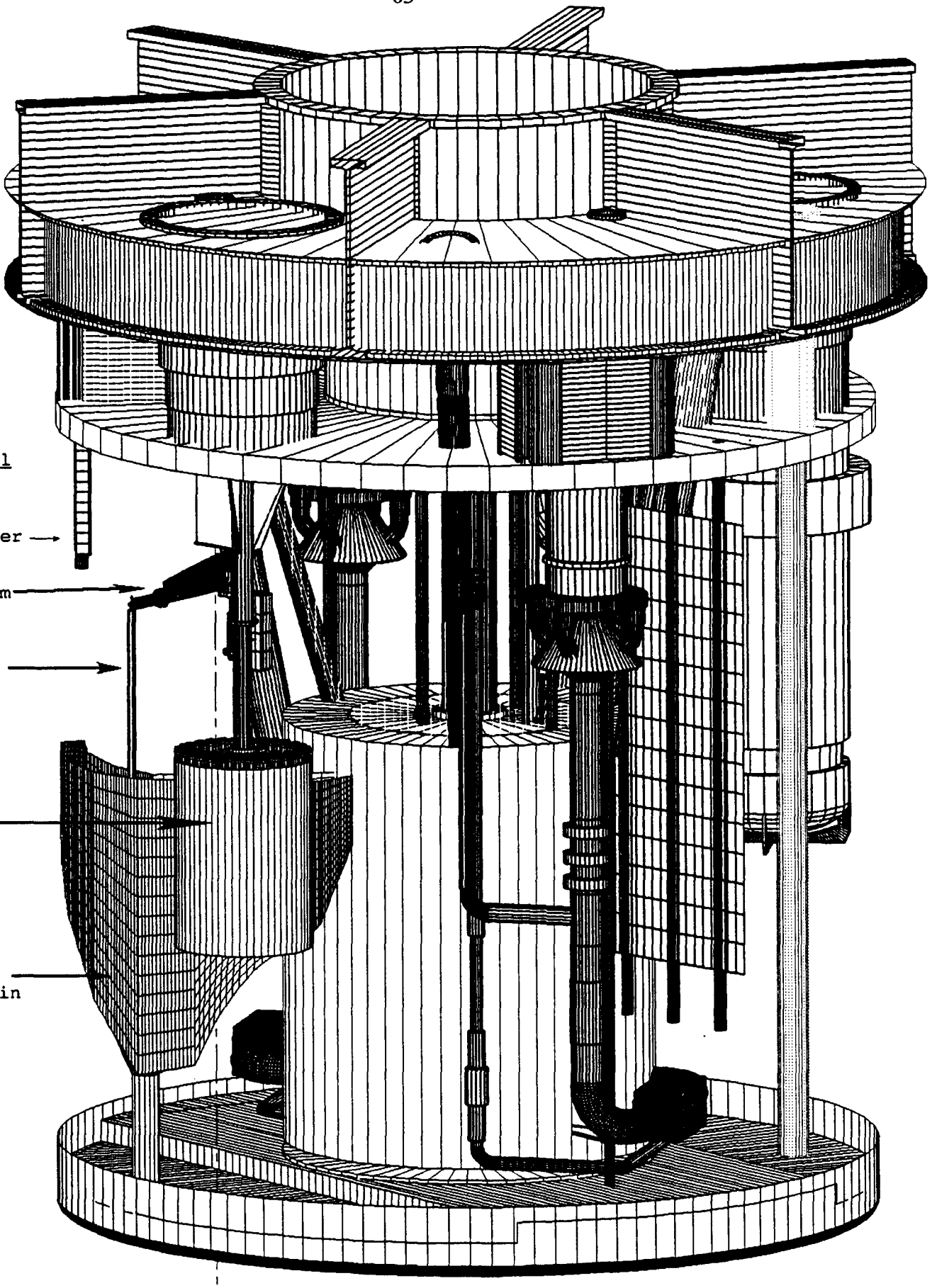


Figure 1: EBR-II Fuel Handling Equipment, View 1.

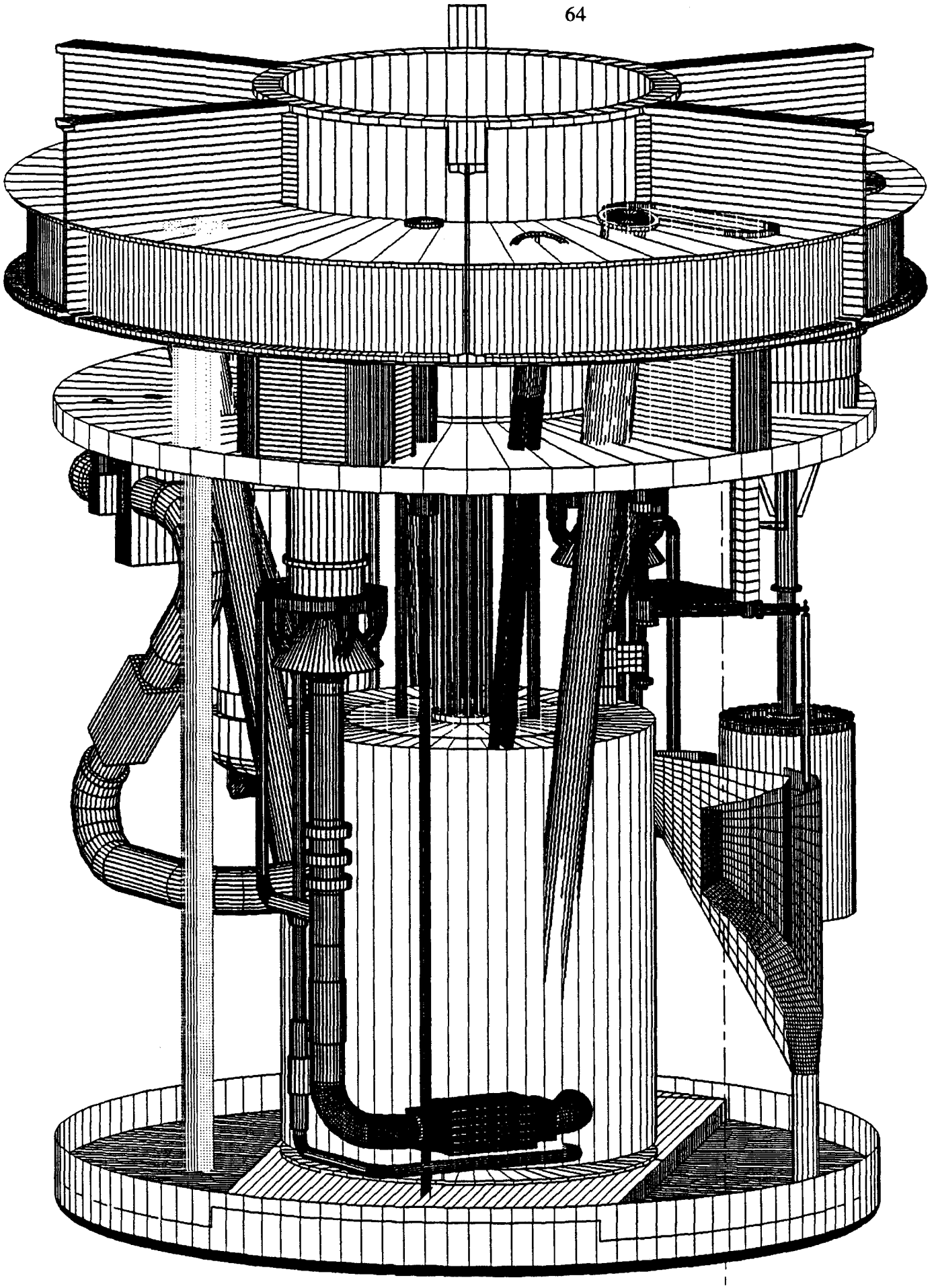


Figure 2: EBR-II Fuel Handling Equipment, View 2.

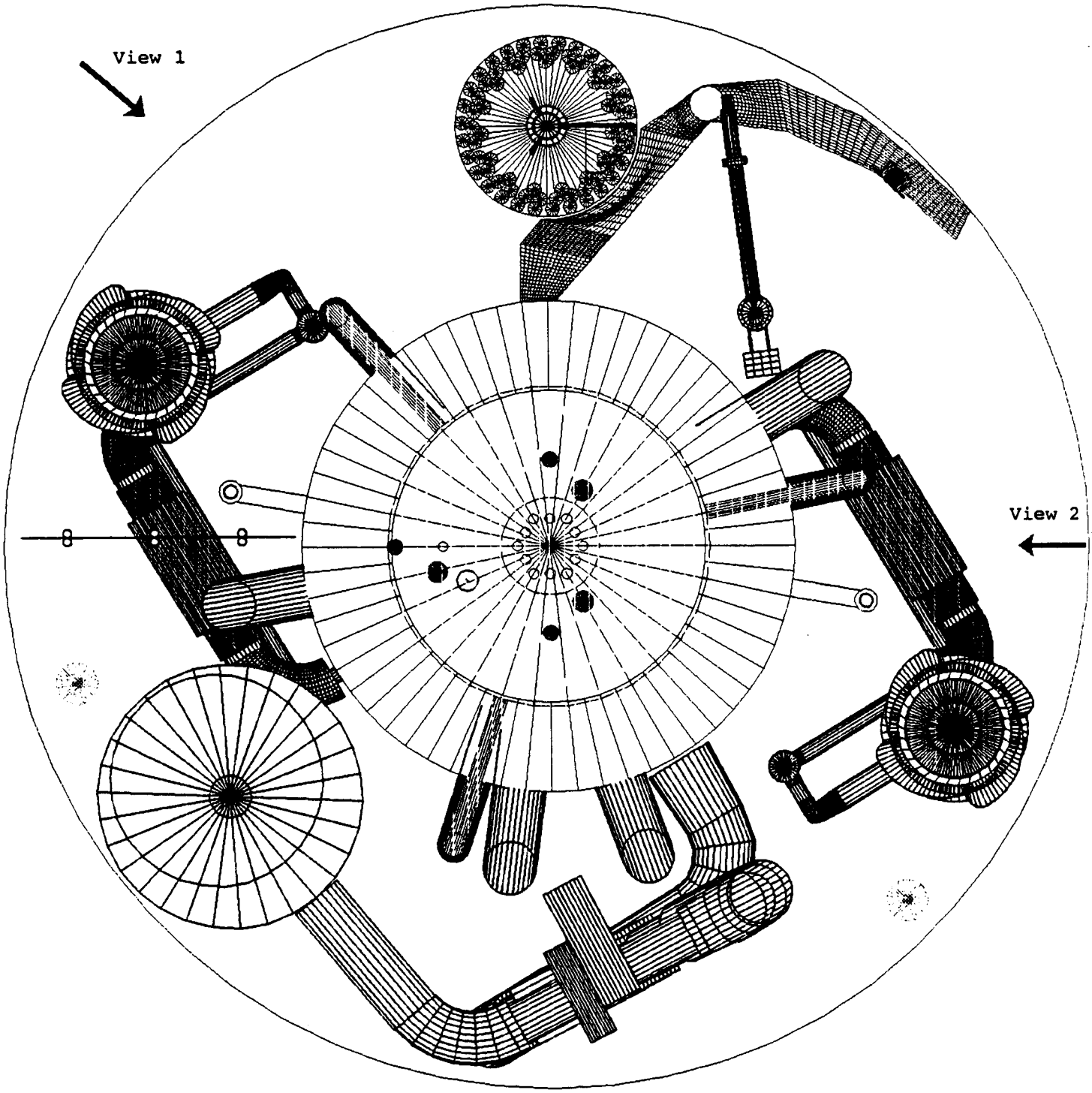


Figure 3: Plan View of the EBR-II Primary Tank, Looking Downward From Sodium Level.

92-048 -- ADVANCED RETORT CONCEPTS FOR LWR ACTINIDE SEPARATION

Associate Laboratory Director Area: Engineering Research

Principal Investigator: R. E. Holtz, Reactor Engineering

Funding History:

FY 1990 $ 0K
FY 1991 $ 0K
FY 1992 $285.3K
FY 1993 $ 0K
FY 1994 $ 0K

Purpose: Actinides from spent LWR fuel can be "burned" in integral fast reactor (IFR) plants to dramatically reduce the duration of the risk to the public from light water reactor (LWR) nuclear waste. Candidate pyrochemical processes have been identified which have the potential to accomplish the LWR actinide separation. Retorts are required in these processes for materials separation. Economic actinide separation by pyrochemical processes requires crucibles that can be constructed in the larger sizes needed for full-scale operation and that can repeatedly withstand the process conditions without degradation. The purpose of this investigation was to determine the current status of materials research and materials compatibility testing for advanced retort concepts, to identify the scope of boiling tests needed to define operating conditions for retorting magnesium-zinc solutions, and to develop technically feasible concepts that have the potential to be employed for these retorts.

Approach: Materials investigations and cadmium boiling tests, performed as part of the development of the Cathode Processor for the Fuel Cycle Facility of the Integral Fast Reactor/EBR-II, provided part of the background resource drawn upon to investigate advanced retort concepts for LWR actinide separation. This was complemented by the extensive theoretical analyses and investigations of liquid-metal boiling performed during development of the Liquid Metal Fast Breeder Reactor. Literature searches completed the information base for this work.

LWR actinide separation processes were examined to identify anticipated retort operating conditions. Existing and new materials were examined to identify candidate materials compatible with both the process fluids and temperatures of the retorting environment. The state of knowledge of the boiling characteristics of magnesium and zinc was investigated to further define the physical processes occurring within a retort. Information from the investigation of candidate crucible materials, together with estimates of batch volumes, were factored into the development of retort concepts.

A substantial body of information exists on the suitability of numerous materials for containment service in spent fuel reprocessing. These data were examined. The focus was not to define new material development needs, but to identify candidate materials for pyrochemical process crucibles from existing or recently developed materials. Results of extensive materials compatibility testing performed prior to 1970 in support of spent reactor fuel reprocessing identified tungsten and certain tungsten alloys as the only materials known to possess sufficient corrosion resistance to contain zinc and high-zinc alloys. Continued research and development has yielded new and improved materials that are under investigation as candidate containment

materials. These are basically carburized or nitrided refractory metal alloys and ceramic materials. Based on tests at Argonne and elsewhere, Tribocor 532N (50 wt% Nb, 30 wt% Ti, 20 wt% W; surface nitrided) appears to be a promising new candidate for pyrochemical process service.

Little fundamental boiling information is available for magnesium, zinc, or magnesium-zinc solutions. To gain insight into the possible boiling behavior of magnesium and zinc, thermophysical property data for these metals were obtained and compared with corresponding properties of sodium and cadmium. Magnesium tends to wet boiling surfaces, like sodium, and has other properties similar to those of sodium. The boiling behavior of magnesium may therefore resemble that of sodium, which exhibits large incipient-boiling superheats. If zinc tends not to wet boiling surfaces, its boiling behavior may be similar to that of cadmium. However, the complex dependence of liquid-metal boiling on thermophysical properties, extent of fluid wetting, and the character of the boiling surface makes it difficult to predict the boiling behavior of liquid metals with much certainty. A series of boiling experiments has been defined which will generate the needed boiling characteristics for magnesium, zinc, and magnesium-zinc solutions.

The capacity of the process crucible, characteristics of suitable materials of construction, and methods of heating were among the aspects addressed in the retort concept development. The volume of a full-scale process crucible has been estimated to be an order of magnitude larger than that of the crucible being studied for engineering-scale processes. For the magnesium-zinc process, this represents a 200 kg batch of original UO_2 LWR fuel in the full-scale system. The resulting 30-in. diameter crucible exceeds the fabrication state-of-the-art for some possible crucible materials, but appears achievable with Tribocor 532N.

Various heating methods were studied for the furnace region of the retort. Induction heating and thermal radiation heating were selected as the two best approaches. The design of a production-scale induction-heated furnace was based on experience accumulated in the development of the Cathode Processor for the IFR Fuel Cycle Facility. In this concept, a passively cooled copper induction coil is used. A graphite furnace liner acts as a susceptor, heating the crucible by thermal radiation. The furnace liner and process crucible remain unchanged in the thermal-radiation heated furnace concept. A set of refractory-metal heating elements replaces the induction heating coil. Both retort concepts appear technically feasible.

Technical Progress and Results: Materials were examined for use in retorting operations for LWR actinide separation. Candidate materials for retort crucibles and crucible coatings include tungsten, certain ceramic oxides, and some carbides or nitrides of refractory alloy base metals. Tribocor 532N appears to be a promising crucible material that could be fabricated in the sizes projected for production-scale crucibles, and was selected as the crucible material for the two retort concepts developed in the project.

The development of fundamental boiling characteristics for magnesium and zinc was identified as a key research need in support of LWR actinide separation. Thermophysical properties of magnesium and zinc were compared with those of sodium and cadmium to project the anticipated boiling behavior of magnesium and zinc. A series of boiling experiments needed to determine the effect of power input, pressure-temperature history, and gas content on the boiling

characteristics of magnesium, zinc, and magnesium-zinc solutions was identified. These experiments, necessary to define the conditions for successful retort operation, are planned to be conducted in future work.

Two retort concepts which appear technically feasible have been identified and studied. They are 1) the induction heating concept with a passively cooled induction coil which has a graphite furnace liner acting as a susceptor, and 2) the thermal radiation heating concept using refractory metal heating elements. These two concepts are illustrated in Figures 1 and 2, respectively. Further development of these two retort concepts is included as a subsequent effort.

Specific Accomplishments: An internal report describing the FY 1992 work has been prepared.

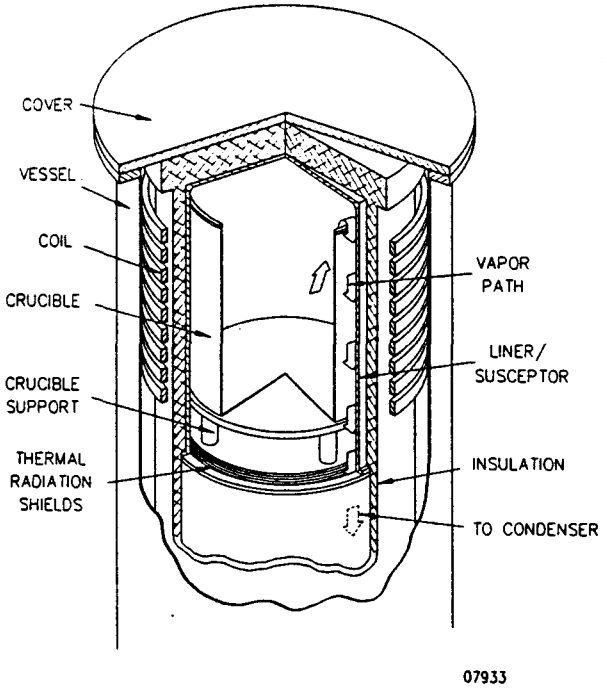


Fig. 1 Induction Heating Concept

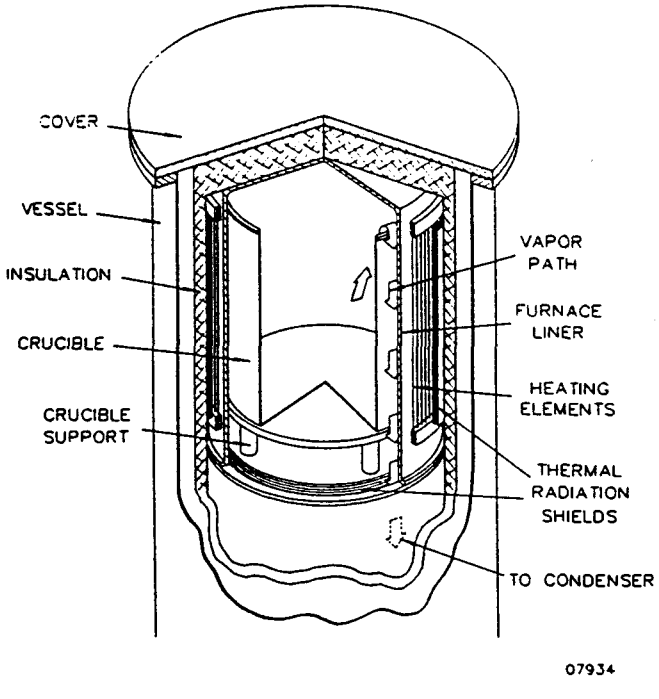


Fig. 2 Thermal Radiation Heating Concept

92-052 -- SPACE EXPLORATION RESEARCH

Associate Laboratory Director Area: Engineering Research

Principal Investigators:
S. K. Bhattacharyya, Engineering Physics
Basil F. Picologlou, Engineering Physics
Larry W. Carlson, Engineering Physics
Ankur Purohit, Engineering Physics
M. H. Bhattacharyya, Biological & Medical Research
L. A. Neimark, Materials & Components Technology
Paul Raptis, Materials and Components Technology
Nelson A. Hanan, Engineering Physics

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$191.8K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: To perform the assessment, evaluations and preliminary laboratory work necessary to undertake detailed R&D work at ANL in support of the development of nuclear propulsion and related technologies. These technologies play a key role in the National Space Exploration Initiative (SEI).

Approach: The Space Exploration Initiative represents the next major thrust in space by the U.S. In order to meet the goals of the proposed missions, significant advances have to be made along a number of broad technology fronts.

The aim of this work was to perform the initial analysis and preliminary R&D work in the areas described below to better position the Laboratory in the required long-term research and development effort needed in the future. The work was performed by investigators from several divisions.

Technical Progress and Results: A summary of the results obtained in each of the areas investigated in this project is given below.

a. Preliminary Design of Cermet Reactors for Nuclear Thermal Propulsion Systems: In the 1960s ANL developed a design for a cermet reactor to be used for nuclear thermal propulsion. In this project, confirmatory neutronic and thermal-hydraulics analyses for the ANL-designed cermet reactor (designed in the 1960s) were first performed using state-of-the-art computer codes, and the results basically confirmed those presented in the previous ANL work.

Based on that previous ANL-design and in some more recent development in the industry, two new prospective designs were generated and analyzed in this project. In both of these designs a fast spectrum hydrogen cooled reactor is used. The reactor core in both designs produces about 1600 MWt of power, and provides a thrust equal to 75,000 lbf and specific impulse of 860 and 900 sec. The thrust-to-weight ratio in both designs is greater than 5.0. The important

characteristics of these designs (thrust-to-weight ratio and specific impulse) are comparable to other designs being developed by other reactor designers.

In conclusion, the preliminary designs performed during this project show that cermet designs look attractive for more detailed design and analysis. Note that at present there is industrial interest in cermet reactors for nuclear thermal propulsion (e.g. Pratt & Whitney concept for the Space Exploration Initiative (SEI)).

b. Code Development to Study Fuel Cell Systems: The Argonne Solid Oxide Fuel Cell (SOFC) is being considered for a space application wherein it would be used to generate peak electric power during the lunar night. Many other applications have also been proposed for the SOFC in the space arena.

In this project, two computer programs were developed for the SOFC to predict initial-transient-to-steady-state thermal hydraulics coupled with its electrochemical characteristics. The first computer program "SOFCTRAN", analyzes the power generation mode of operation , and the second code "SOFCREGN", predicts fuel cell regeneration characteristics. A preliminary analysis for a specific design for 6 kW of power was also performed.

Note that there are currently two small externally funded efforts in this area (funding received after the LDRD project phase).

c. Use of ^{41}Ca to Study Bone Loss in Astronauts during Spaceflight: One of the major issues regarding long term space missions is the effect of microgravity on the physiology of astronauts and their ability to function during the flight and at the destination. Significant bone loss has been shown to occur in astronauts during space flights. These data have been confirmed by cosmonaut experience in the FSU. Research has been conducted with rats and has indicated that bone formation ceases within two weeks of the start of flight while bone resorption continues at pre-flight levels. Human studies are needed to understand the mechanics of the bone loss in order to devise measures to counteract bone loss. To date good human studies have not been possible because of the lack of sensitive assay techniques. Recently a very sensitive array for ^{41}Ca has been developed using accelerator mass spectroscopy by ANL and Purdue University scientists. This technique has been examined and shown to be very promising for human studies with astronauts.

d. Testing of Hydrogen-Cooled Fuel Elements for Space Reactors in the Transient Experimental Test Reactor (TREAT): The feasibility of testing hydrogen-cooled fuel elements for Nuclear Thermal Propulsion reactors in TREAT was examined. It was determined that the TREAT reactor can provide energy deposition rates that will allow testing at prototypic fuel temperatures and reduced coolant flow rates for test durations of the order of one minute. The available test space in TREAT allows testing of entire fuel elements in test vehicles inserted in the core and connected to coolant and instrumentation lines at the top, making installation and removal simple. The required hydrogen coolant system is straightforward and can be engineered to satisfy any safety requirements through well established rules on design and operation of hydrogen systems. A once-through loop with fission products removal before disposal through burning was chosen for simplicity and ease of operation. The available test space allows multiple containment of

hydrogen in the test vehicle to make hydrogen release in the reactor itself not credible. Note that if the required system is installed, TREAT can compete with the capability available at the Impulse Graphite Reactor (IGR) in Russia.

e. Assessment of the Solid Fuels Development for Thermal Propulsion for Space Reactor Applications: A review of the literature for two types of fuels for solid cores for the Nuclear Thermal Propulsion systems was performed. The first fuel type is based on carbide fuel particles embedded in graphite matrix, and the second fuel type -known as cermet fuel- consists of oxide fuel particles embedded in refractory metal matrix. The bulk of the work in the development of these fuels was started in the late 1950s and ended in the early 1970s; some work on the cermet fuels was also performed in 1985-1987. The major conclusions in the work performed for this project are: i) the programs were a complete technical success at the time of termination; ii) fabrication technology for both types of fuel were mastered and the knowledge and experience is still available; iii) hydrogen attack on graphite- and all carbide-based fuels was systematically reduced by ingenious innovations and clever design, but it was not completely eliminated; iv) cermet fuels had reached a state of maturity based on which it is reasonable to state that with some additional work, one can design and fabricate a self-contained core in which fission gases released to the environment could be minimized; and v) it is recommended that significant national future effort in fuel development for thermal propulsion reactors be directed toward qualifying cermet fuels.

f. Instrumentation: An evaluation of capabilities (within ANL) to develop instrumentation for high temperature measurements and remote sensors for lunar/Martian or satellite atmosphere was performed. This evaluation led to the conclusion that ANL is well positioned to contribute to the development of sensors/instrumentation for high temperature measurements. For the remote sensing ANL has some expertise but it is recommended that cooperation with the weapons laboratories is the best way for ANL participation in this area.

Specific Accomplishments: Internal technical memos were prepared in the different areas addressed in this project. Also computer codes were developed to study Solid Oxide Fuel Cell power systems.

91-105R1 -- ACTINIDE RECYCLE DEMONSTRATION - PROCESS DEVELOPMENT FOR RECOVERY OF OXIDE-REDUCTION SALTS

Associate Laboratory Director Area: Engineering Research

Principal Investigator: J. E. Battles, Chemical Technology Division
C. C. McPheeters, Chemical Technology Division

Funding Profile:

FY 1990	$ 0K
FY 1991	$247.2K
FY 1992	$204.3K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: Determine engineering practicality by assessing limiting conditions for the recovery of salts from oxide-reduction operations using the electrochemical technique previously shown to be technically feasible and to devise a method to control the dust from flaking off the carbon anode, which has been observed to short circuit the electrochemical cell.

Approach: To determine the limiting current condition under which the $CaCl_2$ in the salt begins to decompose, the small-scale cell was modified to collect the gases released at the carbon anode. These gases are analyzed to determine when chlorine from $CaCl_2$ was first released.

As an alternative method for collecting the dust, an effort was made to sweep the carbon particles away from the carbon electrode by flowing the molten salt upward along the anode surface, then diverting the salt away from the anode and downward by gravity through a filter. The motive force for flowing the molten salt upward was provided by bubbling inert gas into a fairly narrow annulus around the carbon anode. This annulus was formed between the carbon anode and a ceramic tube that surrounded the anode. The anode was hollow to provide a passage for the inert gas to flow out the bottom, so that gas bubbles rising through the annulus would sweep molten salt electrolyte along with them. At the top of the ceramic tube, the salt overflows into a filter and slowly drains back into the electrolyte pool. The carbon particles collect in the filter. A schematic drawing of this concept is shown in the attached figure.

Technical Progress and Results: An experiment was designed and performed to determine how high the upper limit of the operating cell voltage could be extended without causing significant decomposition of $CaCl_2$ salt. In most of the previous electrolysis experiments, the operating cell voltage had been limited to less than 2.7 V, the reversible decomposition potential for $CaCl_2$ with a zinc cathode. In this experiment, the upper limit of operating cell voltage was increased to 4.8 V (the reversible decomposition potential of CaF_2).

This experiment was designed to collect samples of product gas from the anode compartment and to determine if there was any detectable chlorine in the gas samples collected in the operating cell voltage range 2.7-4.8 V. The main body of the gas-collector system was a quartz bell jar enclosing the anode and the MgO shroud. The bell jar was sealed at the bottom by emersion in the molten salt.

A current density of 840 mA/cm^2 was obtained at 4.8 V, and there was no evidence of $CaCl_2$ decomposition until nearly all the CaO had been consumed. Initial engineering calculations concluded current densities on the order of 500 mA/cm^2 or more are desirable for salt recovery in the Actinide Recycle Process. The gas analyses were inconclusive because they indicated that complicated reactions involving anode product gases and the materials of the gas collector system (including quartz tube, molybdenum rods, and steel fittings) had occurred. Therefore, to avoid such reactions, a plain graphite gas collector anode was designed. The components of the gas-collector system are all made of graphite. Only the lower part of the inner surface of the graphite bell jar will serve as the anodic reaction surface, the outside surface of the bell jar is insulated with a tight-fitted MgO crucible. The anode product gases that accumulate in the top void space of the bell jar during electrolysis will pass through the graphite tube channel and enter directly into the pyrex gas sampling bottle. Therefore, the design is expected to eliminate the possibility of reactions involving the anode product gases and the materials of the gas collector system, and thus the gas samples collected will be more representative of the anode product-gas compositions at the specified electrolysis conditions.

Two electrolysis experiments were performed to demonstrate the concept for in-situ removal of carbon electrode dust from molten salt electrolyte. Bench simulation experiments had been made to establish the basic parameters for the cell set-up and to determine the sparging gas flow rate required to provide adequate motive force for flowing the molten salt electrolyte upward in the annulus between the graphite rod anode and the anode shroud.

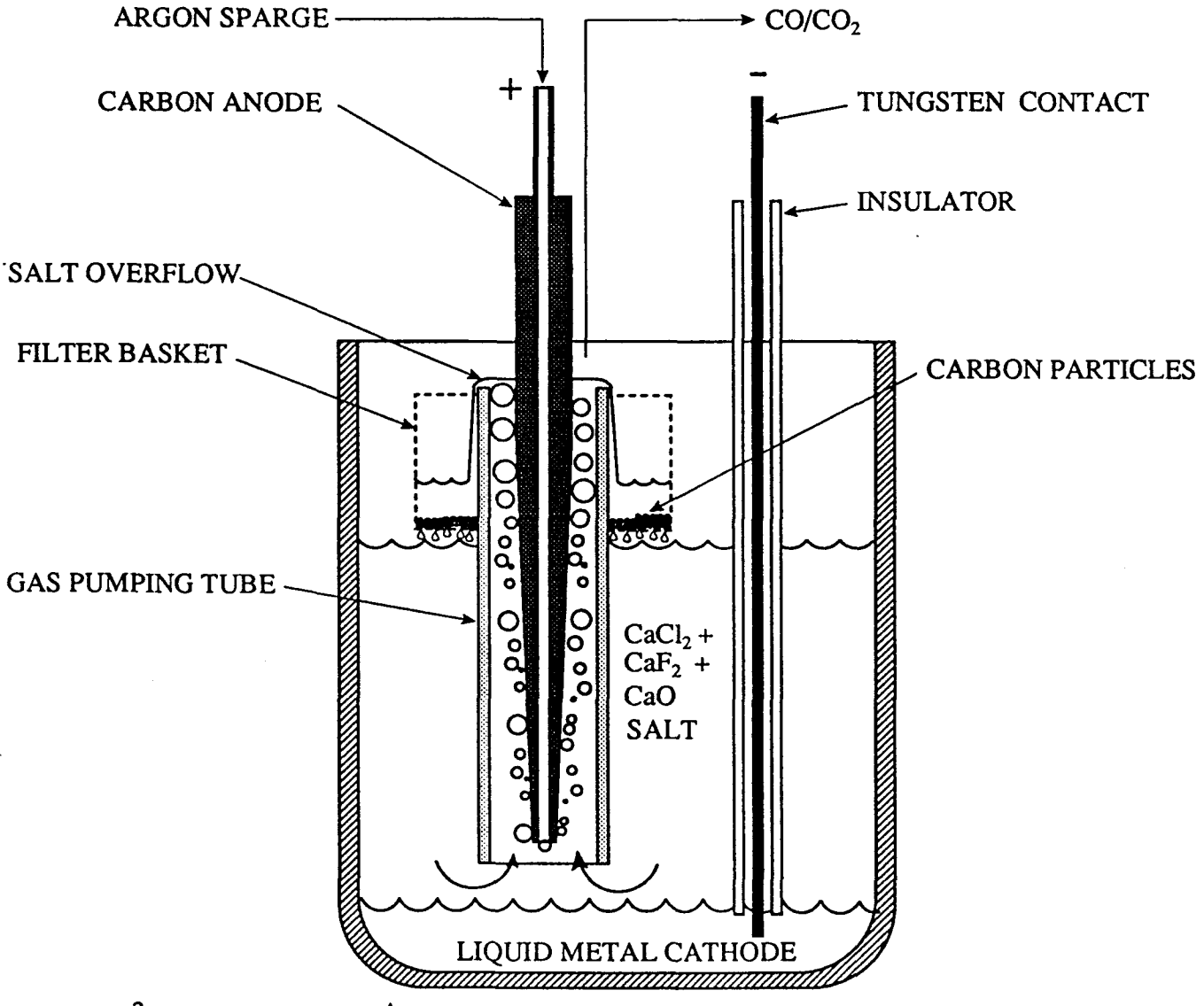
The results of these experiments showed that although a significant amount of carbon powder could be retained inside the porous MgO catch-basket attached to the anode shroud, there was still a large amount of carbon dust dispersed into the bulk salt in the cell container of the sweep gas which exited the bottom of the shroud carrying carbon into the bulk salt. The current efficiency obtained for these two experiments was low, only about 10%. Therefore, to improve the performance of electrolysis, significant modifications of the cell dimensions would need to be made for future experiments.

Specific Accomplishment: It was shown that current densities of as much as 840 mA/cm^2 can be accomplished without significant decomposition of the base salt until nearly all the CaO has been decomposed. Toward the end, however, significant salt decomposition was observed. An improved design of graphite anode-gas collector electrode has been made to avoid chemical interactions, which prevented accurate determination of anode gas composition in the first test. The general feasibility was demonstrated of the in-situ circulation and filtration of electrolyte for carbon removal, but the parameters affecting gas pumping must be adjusted to promote only upward salt flow inside the shroud.

Publications Include:

1. CMT Monthly Reports:
   ANL-CMTI-10531 (Feb. 92) ANL-CMTI-10631 (July 92)
   ANL-CMTI-10603 (June 92) ANL-CMTI-10650 (Aug. 92)
2. Invention Report, "Method for In-Situ Removal of Electrode Dust from Liquid Electrolytes," ANL-IN-92-20, In preparation.

CALCIUM ELECTROWINNING WITH CARBON COLLECTION (SPARGED ANODE CELL WITH FILTER)



Anode: $O^{2-} + C \longrightarrow CO\uparrow + 2e^-$

Cathode: $CaO + 2e^- \longrightarrow Ca + O^{2-}$

92-177 -- ALTERNATIVE REDUCTANT AND SALT SYSTEMS FOR REDUCTION OF TRU OXIDES

Associate Laboratory Director Area: Engineering Research

Principal Investigator: J. E. Battles, Chemical Technology
C. C. McPheeters, Chemical Technology

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$215.7K
FY 1993	$230K
FY 1994	$ 0K

Purpose: To explore alternative reductants and salt systems for the reduction of transuranic oxides and recovery of the transuranic elements (neptunium, plutonium, americium, and curium) for feed to the IFR pyrometallurgical process for metal fuels. The goal is to identify a process with potential for operation at lower temperature (500-600°C), reduced salt volume, and less demanding material requirements that would allow recovery of transuranic elements from waste residues and hence, minimize the waste disposal problems.

Approach: Three conceptual processes are being developed in the Chemical Technology Division of Argonne National Laboratory for recovery of actinide elements from LWR spent fuel: the salt transport process, the magnesium extraction process, and the zinc-magnesium process. These high-temperature processes (~800°C) are largely based on pyrochemical data developed at ANL during the '60s and '70s. In all three processes, the LWR oxide spent fuel is reduced by reaction with calcium metal in a two-phase, liquid metal and molten salt, system. An amount of CaO chemically equivalent to the fuel reduced is formed during the reduction. The CaO must be dissolved in the molten salt ($CaCl_2$-CaF_2), and the salt is recycled by electrochemically reducing the CaO to calcium metal. Oxygen is evolved as CO and CO_2 at a carbon anode. The bulk of the CaO results from reduction of UO_2. The actinide elements are extracted from the liquid metal phase by salt-phase transport in the first concept, and they are extracted by liquid magnesium in the second concept. In the zinc-magnesium process, uranium precipitate is separated from the liquid metal phase and the liquid metal is evaporated from the TRU product. Laboratory-scale experiments have shown each of the three processes to be chemically feasible. Undesirable aspects of these conceptual processes include the high temperature for process operation (800°C), the reduction of all the LWR oxide fuel, which is approximately only 1% TRU oxides, and the robust materials required for the aggressive process conditions.

Our study has focused on two different approaches (1) the use of lithium metal as the reductant with LiCl containing process salts, and (2) the use of $MgCl_2$ to effectively separate minor TRU elements from fuel or waste prior to the reduction. The advantages of using a reductant/salt system such as Li/LiCl-KCl over the Ca/$CaCl_2$-CaF_2 are that much lower operating temperatures (500-600°C), where materials problems are less severe, are possible and the salt composition would be similar to IFR process salt, thus simplifying waste form developement. The second approach is possible because of the solubility difference between plutonium and uranium in

$MgCl_2$. For example, in an equimolar mixture of $MgCl_2$-$CaCl_2$ in equilibrium with PuO_2 the amount of plutonium in solution would be 6.5 wt %, whereas the same mixture in contact with solid UO_2 would contain only 0.025 wt % uranium. The solubilities would probably be higher in pure $MgCl_2$. The reaction, which takes place between PuO_2 and $MgCl_2$, is

$$PuO_2 + MgCl_2 \text{ ---> } MgO + PuOCl + 1/2\ Cl_2. \quad (1)$$

The reaction is not thermodynamically favored having a free energy of reaction at 1000 K of 18.9 kcal mol^{-1}. However, if the chlorine can be removed by using a gettering agent, for example zinc, the free energy of reaction becomes favorable. The soluble PuOCl is very easily reduced, at temperatures less than 800°C.

Technical Progress and Results: (1) First Approach: The results of seven experiments using lithium as a reductant for UO_2 are presented in Table 1. Experience has shown that UO_2 is more difficult to reduce than the TRU oxides and thus, any system which reduces UO_2 should readily reduce these oxides also. The experiments were conducted in MgO crucibles using tantalum stirrers. The variables have been salt composition and temperature. The reduction of UO_2 by lithium is thermodynamically more favorable at 800 K (527°C), $\Delta G°$ = -9.95 kcal mol^{-1}, than it is at 1100 K (827°C), $\Delta G°$ = -2.18 kcal mol^{-1}; however, the kinetics are probably not as favorable at the lower temperature. Because kinetics were expected to be limiting, the first experiments were done at 775°C. An all lithium-based salt was employed to enhance the solubilities of both lithium and the Li_2O reduction product. When this experiment went well, lower temperatures were tried. To achieve temperatures below 650°C, another salt must be added to the mixture. KCl was used in this study. Successful reductions were achieved in each experiment over the entire temperature range of 775 to 500°C. Residual UO_2 was below detection limits in all of the reduction products.

LiF may prove troublesome in proposed waste forms; therefore, one experiment was attempted at 500°C with a LiCl-KCl salt without LiF. This experiment also was successful. At the lower temperatures, the solubility of Li_2O is low in LiCl-KCl. In some cases, the excess Li_2O formed a ring on the crucible wall and entrapped some of the uranium product. Because of this, the quantity of salt was increased in the last two experiments; this resulted in cleaner salts and no entrapped uranium.

A 100% excess of lithium reductant was used in most of the tests, which resulted in lithium coating on the uranium product. The one 500°C test that employed only 16% excess lithium resulted in a good reduction. Because any excess lithium beyond that required to saturate the salt should have no additional beneficial effect, this result was expected. In this test, all the excess lithium was in solution in the salt, and lithium was avoided on the uranium product.

Analytical assessment indicates other salt additives should be better than KCl for lowering the melting temperature of the salt while maintaining Li_2O solubility. $SrCl_2$ appears to be a very attractive possibility.

(2) Second Approach: The $MgCl_2$ extraction of plutonium was tried on a mock LWR fuel. The mock fuel is a high-fired mixture of UO_2-PuO_2 with added fission products. The extractions were

conducted for 6 h in MgO crucibles at 800°C, using 100 g of fuel, tantalum stirrers, and zinc as a chlorine getter. The amount of plutonium extracted varied slightly depending on sample preparation (35% for fuel ground to ~100 mesh, 38% for fuel ground to less than 400 mesh and 46% for fuel which had been air oxidized to U_3O_8-PuO_2). These results are discouraging for developing a process to extract TRU elements from reactor fuel. Grinding the fuel to a very fine particle size (5-10 microns) may, however, make the plutonium more readily accessible for extraction.

One experiment was run to apply the approach to Rocky Flats ash heel, which is a major defense residue. The contained plutonium was much easier to extract, 93% of the plutonium being extracted in the first 6 h extraction, and >98% after the second 6 h extraction period. The ash heel is the residue left from nitric acid extraction of raw ash, and contains ~11% PuO_2 in a matrix of SiO_2 and metal oxides. This material had been calcined, ground, and blended at Lawrence Livermore National Laboratory in an effort to produce a uniform sample. The particle size of this material is ~20 microns. This result looks very promising as a means of extracting residual plutonium from ash heels and may be applicable to other waste forms as well.

Specific Accomplishments: Complete reductions of high-fired UO_2 were demonstrated at temperatures down to 500°C using lithium in the presence of a LiCl salt. When the salt contains little excess lithium, a clean uranium precipitate is obtained; at higher lithium concentrations, a lithium coating was found on the uranium. It is desirable to have sufficient salt to dissolve the Li_2O reaction product, and a low-temperature salt that is expected to have high Li_2O solubility has been identified.

A second approach to improving reductions by selectively extracting the TRU actinides from UO_2 fuel into a salt from which they are then easily reduced was only partially successful and does not look attractive for process application. However, the approach was successful in extracting plutonium from an important Rocky Flats residue and should be pursued.

Publications: The work was documented in internal monthly reports of the Actinide Recycle Group. The most information is in the April and May reports, ANL-CMTI-10563 and -10579, respectively. A patent will be sought for the salt extraction of plutonium from ash, and another is expected when the lithium reduction step has been worked into a process scheme.

TABLE 1. Lithium Reductions of UO_2[a]

Exp. No.	Salt	Temp, °C	Observations
AR-148	LiCl = 250 g LiF = 13.2 g	775	Large uranium beads, completely white salt, excess lithium on surface.
AR-149	LiCl = 220 g LiF = 11.6 g	650	Medium uranium beads, completely white salt, excess lithium on surface.
AR-152	LiCl-KCl = 250 g LiF = 13.1 g	650	Li_2O precipitated on crucible wall, small uranium beads coated with excess lithium.
AR-155	LiCl-KCl = 250 g LiF = 13.1 g	550	Li_2O precipitated on crucible wall, white salt and grey salt layers, small uranium beads coated with excess lithium.
AR-157	LiCl-KCl = 250 g LiF = 13.1 g	505	Same as AR-155.
UR-1	LiCl-KCl = 375 g LiF = 13.1 g	500	Less Li_2O precipitation on wall, no grey salt, lithium not stuck on uranium beads which were very fine.
UR-7	LiCl-KCl = 375 g	502	No precipitated Li_2O on crucible wall, no grey salt, excess lithium on surface, uranium beads very fine.

[a] The feed was 50.0 g UO_2. Each reduction except UR-1 used 10.3 g Li (a 100% excess). UR-1 used 6 g Li (a 16% excess).

92-004 -- STRUCTURE AND STABILITY OF CARBIDE/CARBON MATERIALS AT HIGH TEMPERATURES

Associate Laboratory Director Area: Physical Research

Principal Investigator: P.A. Montano, Materials Science.

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$151.5K
FY 1993	$140K
FY 1994	$140K

Purpose: To investigate the x-ray optical properties of metal/carbon multilayers. Our emphasis is on understanding the stability of the interfaces and the correlation between the structural and x-ray optical properties. Our objective is to develop multilayer components to be used as wide band filters and focusing devices in the hard x-ray region. A major application of multilayer optics is as pre-monochromators in high heat load environments.

Approach: Multilayers are becoming popular as optical components in x-ray applications. To obtain the desired properties, the multilayers must be made of elements with a significant difference in their electron densities (e.g., W/C, Si/C, W/Si etc.). It is very important to emphasize the need to have multilayers with very low interfacial roughness. The periodicity, Λ, of the multilayer will determine the range of x-ray wavelengths where this device can be utilized. Multilayer periodicities that can be used in the hard x-ray region have already been prepared. High quality multilayers can have high reflectivities, of the order of 70 to 80 %. The energy bandwidth of such devices can range from $\Delta E/E=5\bullet10^{-3}$ to 10^{-1}. The multilayers do not achieve the same degree of energy resolution as the one obtained with conventional Si or Ge crystals. However, one has a larger energy bandwidth, a fact that can be very useful when the number of impinging photons is critical to the success of an experiment. A low energy resolution multilayer monochromator in the 6 KeV range was successfully used by Stephenson at beam line X-20 at NSLS.

One of the major applications of multilayer optics is as pre-monochromators in high heat load environments. Such a situation will be found at the Advanced Photon Source beam lines. One of the challenges is the construction of a focusing device using multilayer optics. We are testing such an idea by using mica, oriented graphite and very thin Si as substrates. X-ray reflectivity is used to test the optical properties of the multilayers.

Technical Progress and Results. We measured during the last year the structure of Si/C multilayers grown on two different types of substrates, α-Al_2O_3 and float glass. We investigated the effect of substrate and temperature on the quality of the multilayers. In the following paragraphs a brief of summary of some of our results is given.

The reflectivity from a real surface departs from the Fresnel law $R_f(\theta)$ when the surface is not ideally flat. The presence of roughness modifies the type of equations that are needed to analyze the reflectivity. The theoretical reflectivity is fitted to the experimental data to obtain information on the electron density composition of the layers and the normal roughness at the interfaces. In our analysis the theoretical fit will be valid over all angles since we are solving the full dynamical problem, no kinematic approximation was taken. In our measurements we selected an x-ray energy of 24.5 keV in order to completely neglect absorption effects.

One sample consists of 30 bilayers of [Si(10 Å)/C(20 Å)] on α-Al_2O_3. In the analysis of the data, thickness of the bilayers Λ is assumed to be linearly decreasing from the substrate to the top layer with $\Delta\Lambda/\Lambda = \pm 7\%$ and the thickness ratio d_{si}/d_c is kept constant. This was found to give the best fit to the experimental data. The roughness between silicon and carbon, and the electron density of silicon and carbon are assumed to be constant throughout all the 30 layers. The divergence of the incident x-ray beam was found to be $\Delta\Theta_i = 0.005°$ and was taken into consideration in the analysis of the data. The variation of the total thickness is also introduced in the analysis by assuming a Gaussian function with standard deviation σ_D. The best fit was accomplished with σ_D=10 Å. The electron density of silicon and carbon are about 3% and 15% less than their nominal bulk values. The roughness at the silicon carbon interface is only 0.5 Å indicating a very sharp interface in the Si/C multilayer, partly because of the amorphous nature of the Si and C layers. A multilayer with such a small interface roughness is an important physical system, and of great use for optical components. It is an ideal model for the study the nature of interface bonding and roughness.

The second multilayer sample originally consisted of 30 bilayers of Si(25 Å)/C(25 Å) on α-Al_2O_3 that was heated up to 873 K under UHV conditions. In this case it was absolutely impossible to fit the data without the presence of a silicon carbide interface. In the analysis of the data the thickness of the bilayers Λ is found to be monotonically increasing from the substrate up to two thirds of the total thickness, about $\Delta\Lambda/\Lambda$= 13 %, and then decreasing slightly by 0.5 % up to the top layer. The thickness ratios were kept constant during the analysis.

SiC layers were formed as the result of an interface reaction during heating of the sample. The structure now consists of 30 bilayers of [Si(12 Å)/SiC(10 Å)/C(13 Å)/SiC(10 Å)]. A good agreement is observed between theory and experiment for the secondary fringes produced by the interference of reflected waves from the substrate and the total thickness of the multilayers. A surprising result is that in spite of the chemical reaction at the interface, the modulation structure is well preserved with a larger roughness between Si and SiC. The electron densities of Si, SiC, and C are about 2%, 3%, and 15% less than their nominal bulk values. The roughness at the Si/SiC interface is σ=5.0 Å. On the other hand, the roughness at the SiC/C interface is only 0.5 Å. This result suggests that Si is more reactive than C at such temperatures. The roughness between Si and the substrate α-Al_2O_3 is also very large (13.0 Å). This is due to the large chemical reactivity at the substrate interface during heating of the sample.

The samples prepared on float glass substrates do not show the high frequency oscillations in the x-ray reflectivity due to the total thickness of the multilayer. Such a result is characteristic

of very rough interfaces between Si and C, and consequently it will make very poor optical components. The multilayers prepared on float glass are not useful for x-ray optical components.

Summary

We have fabricated interfaces of Si/C multilayers grown on α-Al_2O_3. The samples grown on saphire substrates show very smooth interfaces. We have used x-ray specular reflectivity to study the compositional profile of the Si/C multilayers. We were able to identify the structure of the multilayer interface. We also found the formation of silicon carbide at the interface silicon-carbon after the multilayer is heated in UHV to 873 K. The silicon carbide is formed in the multilayer during heating by interdiffusion of carbon and silicon.

Specific Accomplishments:

To be Published:

Y. Chan, J. Bai,Y. Cao, H. Homma, M. Kentjana, and P.A. Montano,
"X-RAY REFLECTIVITY STUDY OF THE INTERFACES IN Si/C MULTILAYERS GROWN ON SAPPHIRE" (to be submitted)

Conference Presentation:

American Physical Society , Annual Meeting, Indianapolis (March, 1992) ,"X-Ray Reflectivity Study of Si/C Multilayers"

92-023 -- INNOVATIVE THEORETICAL STUDIES IN THE SOLID STATE

Associate Laboratory Director Area: Physical Research

PRINCIPAL INVESTIGATOR: A. A. Abrikosov, Materials Science

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$153.1K
FY 1993	$120K
FY 1994	$ 75K

Purpose: This Proposal takes advantage of visiting, widely-known scientists from republics of the former Soviet Union (FSU), to plant seeds of new programs, based on innovative approaches in theory that are often not used in the U.S. This program allows us also to engage people with a higher level of prior accomplishment in theoretical work than we can normally attract to ANL, and will create new programmatic foundations that combine analytical and computational theory. We hope to continue the new developments with new funding sources and with our existing theoretical staff, as the new methods are transferred to the existing staff.

Approach: Theoretical research that has been funded within MSD by DOE-BES-DMS has generally involved our access to state-of-the-art computers. This work has aided our experimental programs and been well-received in the community, but has not given our theoretical program the highest-level impact that has been achieved in the experimental program. This deficiency has been noted by University of Chicago Review Committees, and others, in the past. In order to give the theory effort a better balance and a strong foundation in true, formal theory, we have initiated this program.

Problems which are being tackled are: 1) interactions across boundaries, treating combinations of layers such as superconductor-normal metal-superconductor, where the normal metal may be magnetic, and combinations where different types of magnetism may exist across the boundaries. The theoretical development is intended to be valid over a wide temperature range, including temperatures far from the relevant ordering temperature (T_c); 2) fluctuation effects in disordered systems to study fluctuational electronic states in materials such as magnetic and liquid semiconductors, amorphous Si and SiO_2, glasses, polymers and substances near a phase transition; and 3) fluctuations in superconductors and their effects on infrared reflectivity and electronic transport, especially along the c-axis of two-dimensional superconductors

Analytic field-theoretic approaches, which are much more correct than earlier semi-classical methods are being used. These are valid away from the pertinent critical temperature(s) and offer the promise of yielding solutions of general applicability with more fundamental insights.

Technical Progress and Results: This LDRD was initiated in FY 1992, and has been successful in attracting three top-level, senior people from the FSU in the targeted areas. A. Buzdin from the Institute of High Pressure Physics and Moscow State University, an expert in interactions across boundaries, and V. Karpov from The University of Saint Petersburg, expert in fluctuations

of disordered systems have already arrived, despite difficulties in finalizing arrangements. A. Varlamov, of the Moscow Institute for Steel and Alloys, will arrive in November to continue his studies of fluctuations in superconductors. Two fine, young theoreticians (A. Tartakovsky and V. Dorin) have been engaged as postdoctoral appointees to enhance the work of the senior personnel.

Karpov has developed a theoretical description of transport properties of liquid semiconductors and proposed experiments which may create n-p junctions from concentration fluctuations in liquid alloys. He helped explain earlier experimental results on the time dependence of pressure-induced changes in amorphous-SiO_2 and conceived specific experiments to test the model. Further indicated studies are being planned with α-quartz., aluminum phosphates and vitreous sulfur

Tartakovsky and the principal investigator have calculated the current-voltage (I-V) behavior in a one-dimensional metal in the case of strong localization; the distribution function of resistivities in a metal wire in the crossover region from weak to strong localization; and rigorously proved localization in a two-dimensional model, without reference to a one-parameter scaling hypothesis. Since Buzdin's arrival, he has given seminars and initiated interactions with experimentalists and other theoreticians in the group.

Specific Accomplishments

Two papers are nearly ready for submittal:

1) M.Grimsditch and V.G.Karpov, "Pressure Induced Transformations in Glasses", and

2) A.Tartakovsky, "Mesoscopic I-V Characteristic of a 1-d Conductor".

92-045 -- LOW-LOSS FLYWHEEL ROTOR USING SUPERCONDUCTING MAGNETIC BEARINGS

Associate Laboratory Director Area: Engineering Research

Principal Investigator: J. R. Hull, Materials and Components Technology

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$ 243.3K
FY 1993	$ 200K
FY 1994	$ 0K

Purpose: The project objective was to fabricate and test a flywheel rotor and associated test apparatus that uses a superconducting bearing, with the potential to achieve a 0.1% per hour bearing loss. The rotor size would be large enough to readily extrapolate the results to commercial flywheel sizes. Successful demonstration of low-friction high-T_c superconducting (HTS) bearings would provide the enabling technology for flywheels used in diurnal energy storage applications, which are of major interest to electric utilities.

Approach: Improved magnetic bearings based on the levitation properties of YBCO superconductors offer the potential to significantly reduce energy losses in rotating electrical machinery and flywheel energy storage systems. HTS flux pinning characteristics allow stable levitation of a rotating bearing, without the position sensors and elaborate feedback control systems that are required for conventional active electromagnetic bearings. It is not necessary to achieve high current transport between the grains of a superconductor to achieve good levitation characteristics, and the inter-granular magnetization properties of melt-textured YBCO materials are adequate for many bearing applications. Technical breakthroughs occurred that enable extremely low rotational losses to be realized with HTS magnetic bearings.

Bearing coefficients of friction (defined as rotational drag to lift force ratio) as low as $3x10^{-6}$ have been measured using small rare earth permanent magnet rotors and YBCO stators, representing an improvement of more than two orders-of-magnitude relative to conventional mechanical bearings and active magnetic bearings. The scope of this investigation was to develop HTS magnetic bearings (through both rotor/stator material and design improvements) that can be scaled for high specific energy flywheel applications with rotational energy losses in the 0.1% per hour range, as contrasted to losses of 1% per hour or more for conventional flywheels.

The project methodology involved the use of a laboratory spin-down test rig to experimentally investigate HTS bearing characteristics such as: geometry and scaling design factors, YBCO levitation improvements, magnet rotor inhomogeneity impacts, and HTS cryo-cooling constraints.

Technical Progress and Results: A superconducting bearing test apparatus was assembled during FY 1992 under the LDRD program, with the potential for testing rotors up to 10 centimeters in diameter. The test apparatus includes a high-capacity diffusion vacuum pump, auxiliary pumps, ionization vacuum gage/controller, liquid nitrogen (LN_2) cooling system, and a 12 in. diameter bell jar test section. The test section (illustrated schematically in Fig. 1) includes a LN_2 cold chamber for cooling YBCO stator elements, positioning devices for proper placement of permanent magnet/flywheel rotor assemblies, mechanisms for flywheel rotor spin-up, and a photocell detector to measure spin-down rpm history. Spin-up tests were accomplished using either a dry N_2 gas jet or a retractable induction motor assembly.

Three different LN_2 cold chamber configurations were fabricated and used in preliminary shakedown tests:

(1) A 5 in. dia. stainless steel cylinder with copper rod cold finger for conduction cooling of the YBCO superconductor located in the vacuum chamber on top of the cold box (see Fig. 1),

(2) A 3 in. dia. brass cylinder and a 1/8 in. thick G-10 fiberglass lid, with the YBCO superconductor located within the LN_2 chamber on a copper pedestal under the lid, and

(3) A 6 in. dia. brass cylinder with a 5 mil thick lid (both mylar and stainless steel shim stock were used in tests) with YBCO elements located within the LN_2 chamber and epoxied to the underside of the lid.

Cold chamber configuration (1) experienced some problems in maintaining a superconducting state for the YBCO elements during gas jet spin-up due to warming by the gas stream being reflected off the rotor. Difficulties were also encountered in maintaining a good vacuum seal between the thin G-10 and mylar chamber lids and the cylinder walls for both configurations (2) and (3). All test rig problems were resolved and bearing shakedown tests completed.

Technical milestones included the successful levitation and spin-up of a 500 gram flywheel assembly. This assembly consisted of a 3.5 in. ring magnet attached to the bottom of a 4 in dia. aluminum flywheel, with a small steel rotor mounted on top for use during induction motor spin-up. Other results during FY 1992 involved characterization and enhancement of rare earth permanent magnets for HTS bearing applications. The azimuthal field inhomogeneities (~5% for commercial magnets) of permanent magnet rotors are known to be responsible for most of the electromagnetic losses associated with HTS bearings. Techniques for improving homogeneity, by superimposing different magnets in layers and the use of ferromagnetic shims, were developed and experimentally verified. Other design enhancements included magnet rotor banding with reinforcing materials to compensate for the low tensile strength of permanent magnets.

During FY 1993, the HTS magnetic bearing R & D activities will continue with emphasis on further friction coefficient reductions and on scale-up to larger rotor/flywheel assemblies. Discussions have been held with electric utilities and industry relative to formation of a flywheel consortium, and utility funding is anticipated later in FY 1993.

Specific Accomplishments: Enhanced HTS bearing spin-down test capabilities were established at ANL and preliminary bearing shakedown tests completed. An invention disclosure for an improved HTS magnetic bearing was filed: "Low-Loss, High-Speed High-Tc Superconducting Bearings" (ANL-IN-92-074) by J. Hull, T. Mulcahy and K. Uherka. A technical publication was prepared: "Improvement of Azimuthal Homogeneity in Permanent-Magnet Bearing Rotors" by J. Hull, T. Rossing, T. Mulcahy and K. Uherka." A Student Research Participation Program report was prepared that described the test apparatus activities: "HTSC Magnetic Bearing Energy Storage Flywheel" by C. Gabrys (Univ. of Vermont). Liaison was established with a number of electric utilities and industrial organizations regarding future joint efforts with ANL in the area of flywheel energy storage.

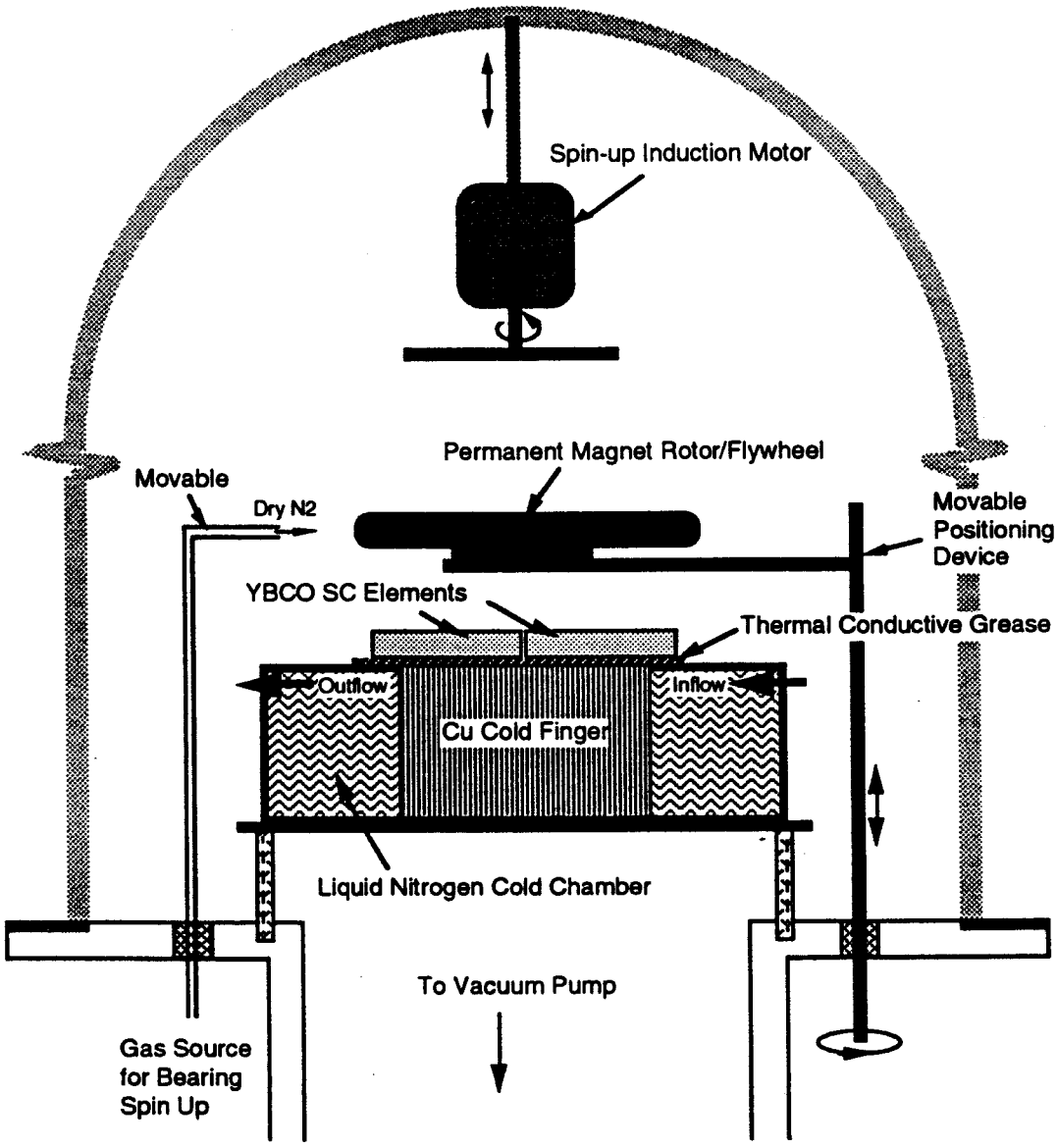


Fig. 1 Schematic of HTS Bearing Test Apparatus

91-016R1 -- INNOVATIVE APPLICATIONS OF HIGH POWER CO_2 AND YAG LASER

Associate Laboratory Director Area: Engineering Research

Principal Investigators: K.H. Leong, Engineering Physics
N. Gopalsami, Materials & Components Technology

Funding Profile

FY 1990	$ 0K
FY 1991	$247.5K
FY 1992	$140K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: Lasers as applied in materials processing have emerged as cost competitive tools in manufacturing. The objective of this work is to exploit ANL's capabilities in innovative application of high power CO_2 and YAG lasers, including beam delivery systems, process control and on-line diagnostics.

Approach: FY 1991 LDRD funding enabled the establishment of a state-of-the-art high power industrial CO_2 and YAG laser facility complete with existing laser workstations and diagnostic equipment.

The use of lasers in manufacturing processes has resulted in improved quality and cost savings compared to conventional methods. This is exemplified by their acceptance as the preferred precision processing tool in sheet metal cutting, welding of automotive parts and heat treating of high wear components. Fit, finish and cost effectiveness are often quoted as the reasons for their common use in the automotive industry.

Rapid acceptance in new applications and other industries have been hampered by the current trend of process development that tends to be very empirical. This is not unusual in the application of an emerging technological tool. Process development will have to be more definitive to overcome the hurdles in technology transfer. What is needed is the comprehension and specification of the process parameters to use in a particular application that is not constrained by a particular laser or processing system. Their major process parameters include beam intensity and beam profile in addition to power. In addition to accurate specification of these parameters, on-line process diagnostics will enable process and quality control.

The focus of this effort is to complete the interfacing of a state-of-the-art digital signal processer (DSP) controller and develop a beam delivery system for the high power YAG laser, and initiate work in several innovative areas that include the accurate measurement of laser beam power, the characterization and optimization of high power laser beam delivery systems, the development of on-line process diagnostics for heat treating and welding and nondestructive evaluation of welds.

Additional participants in this work include Yi Liu, a Postdoctoral Appointee in Engineering Physics, who was responsible for the YAG laser; Donna J. Holdridge, a Senior Technician in Engineering Physics, who was responsible for the CO_2 laser; and H.T. Chien, a Postdoctoral Appointee in Materials Components and Technology, who performed the work on the evaluation of laser processed welds with ultrasonics.

Technical Progress and Results: Interfacing of the DSP controller to the YAG laser was completed. Additional analog outputs were added to the DSP controller to allow control of gas flow for processing and turn-on of diagnostic systems. This DSP controller is a plug-in board to a PC and is very low cost compared to conventional industrial computer numeric controls (CNC). Additional benefits of this DSP controller are high speed and software feedback control capabilities (needed for flexible process control) that are not available on industrial CNCs.

Reflective and transmissive beam delivery optics for cutting, welding and heat treat applications were characterized and compared. Knowledge of their performance characteristics allow the selection and optimization of a beam delivery system for a particular application.

Comparison of instruments for the measurement of power from high power (kW) lasers has been initiated. Manufacturers of different instruments have agreed to participate in this study to determine the precision and accuracy of high power laser measurement devices. It should be noted that no standards exist and National Institute of Standards and Technology (NIST) calibration or traceability is not available for this class of devices.

A laser thermal simulation system (see Fig. 1) using the CO_2 laser and beam delivery optics was set up in collaboration with the Advanced Photon Source to carry out testing of different components and optics that were designed for the 7 GeV beam line. High intensity heat loads comparable to that produced by an x-ray beam were delivered to these components for testing. The success of this method of thermal simulation has resulted in the use of the laser facility by several groups from APS.

On-line process diagnostics development (applicable to welding and heat treatment) was initiated. A study of past research in the field lead to the use of infrared imaging. Initial tests on laser welding showed very promising results where the weld pool can be clearly visualized, and imperfections such as a small (0.1 in. diameter) indentation on one plate or a grain of sand on a plate was easily detectable. Infrared images showing the above mentioned parameters are attached (see Figs. 2-4). Further work is necessary to quantify the infrared signatures for process control or quality assurance.

Work on off-line nondestructive evaluation of welds was initiated using ultrasonics. The results showed that ultrasonics is a very sensitive technique for qualitative determination of such parameters as weld penetration (see Fig. 5). A bad weld could be easily distinguished from a "good" weld. Further work is necessary for a more quantitative evaluation of parameters such as porosity.

Specific Accomplishments: Technology transfer funding has been obtained from DOE/ER through ANL's Technology Transfer Center. CRADAs with Caterpillar and GM AC Rochester Division have been approved by DOE and the companies. An invention report on a means of monitoring the power, profile and quality of the output from a CO_2 or YAG laser has been filed.

Papers:

1. K.H. Leong, Y.Liu and D.J. Holdridge, "CO_2 Laser Beam Propagation with ZnSe Optics," Proceedings of the 11th international Congress on Applications of Lasers & Electro-optics, 25-29 October, 1992 (Orlando, Florida).

2. Y. Liu and K.H. Leong, "Laser Beam Diagnostics for Kilo-Watt Power Pulsed YAG Lasers," Proceedings of the 11th International Congress on Applications of Lasers & Electro-optics, 25-29 October, 1992 (Orlando, Florida).

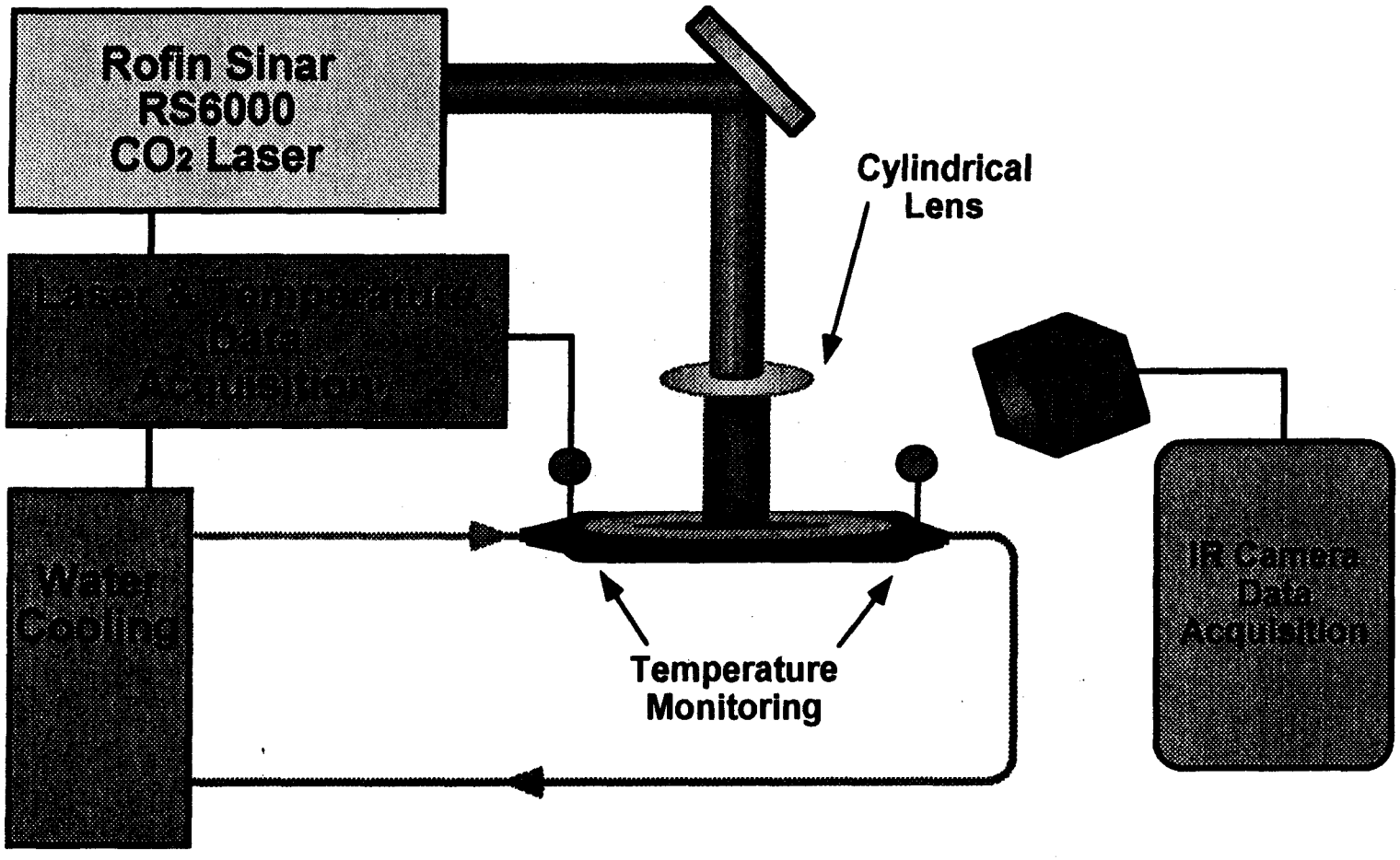


Figure 1. Schematic of laser thermal simulation experiment for testing components designed for The Advanced Photon Source.

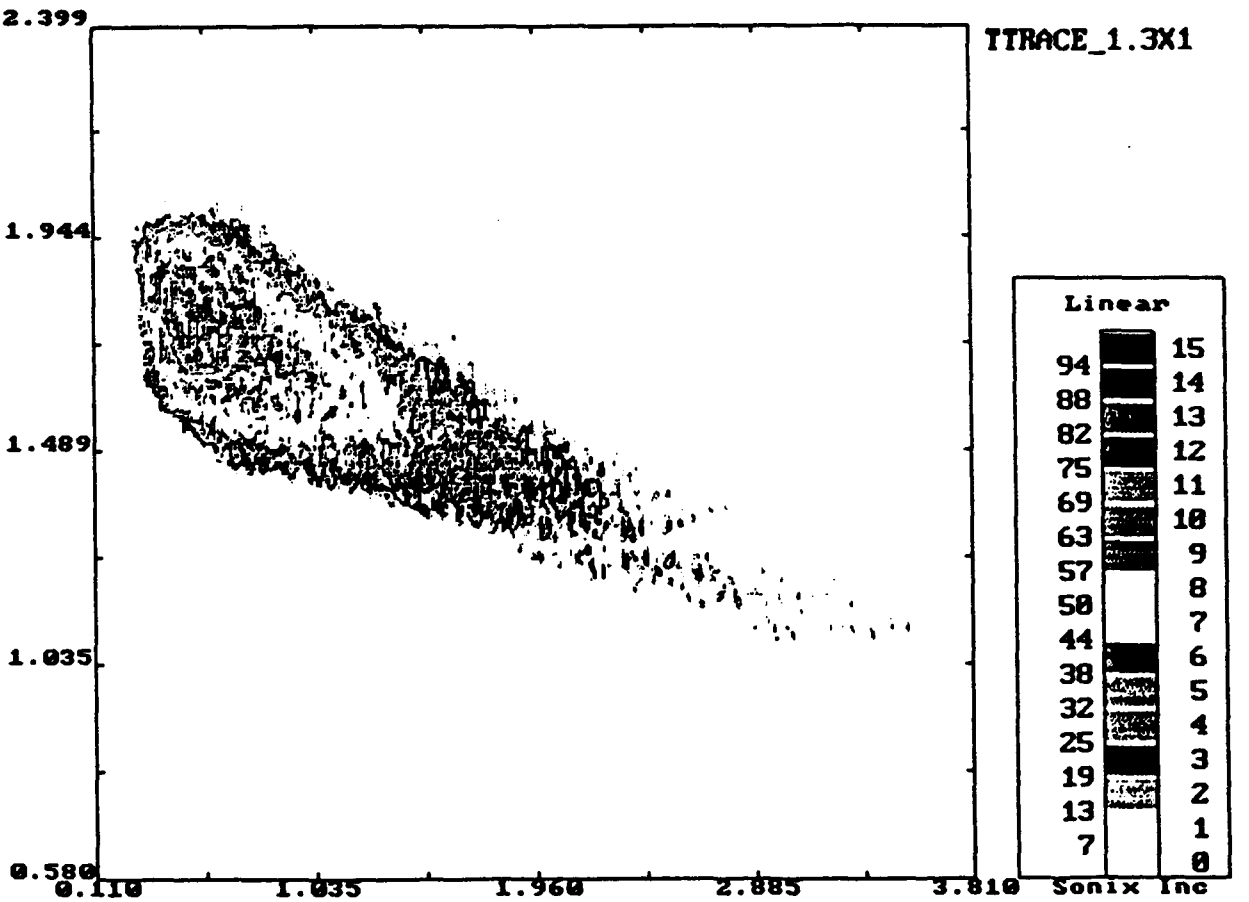


Figure 2. IR image of the surface temperature distribution on a SS sample surface during a 1.6 kw YAG laser welding. The image indicates the shape of the weld pool (on the left) and the contour where solidification occurs.

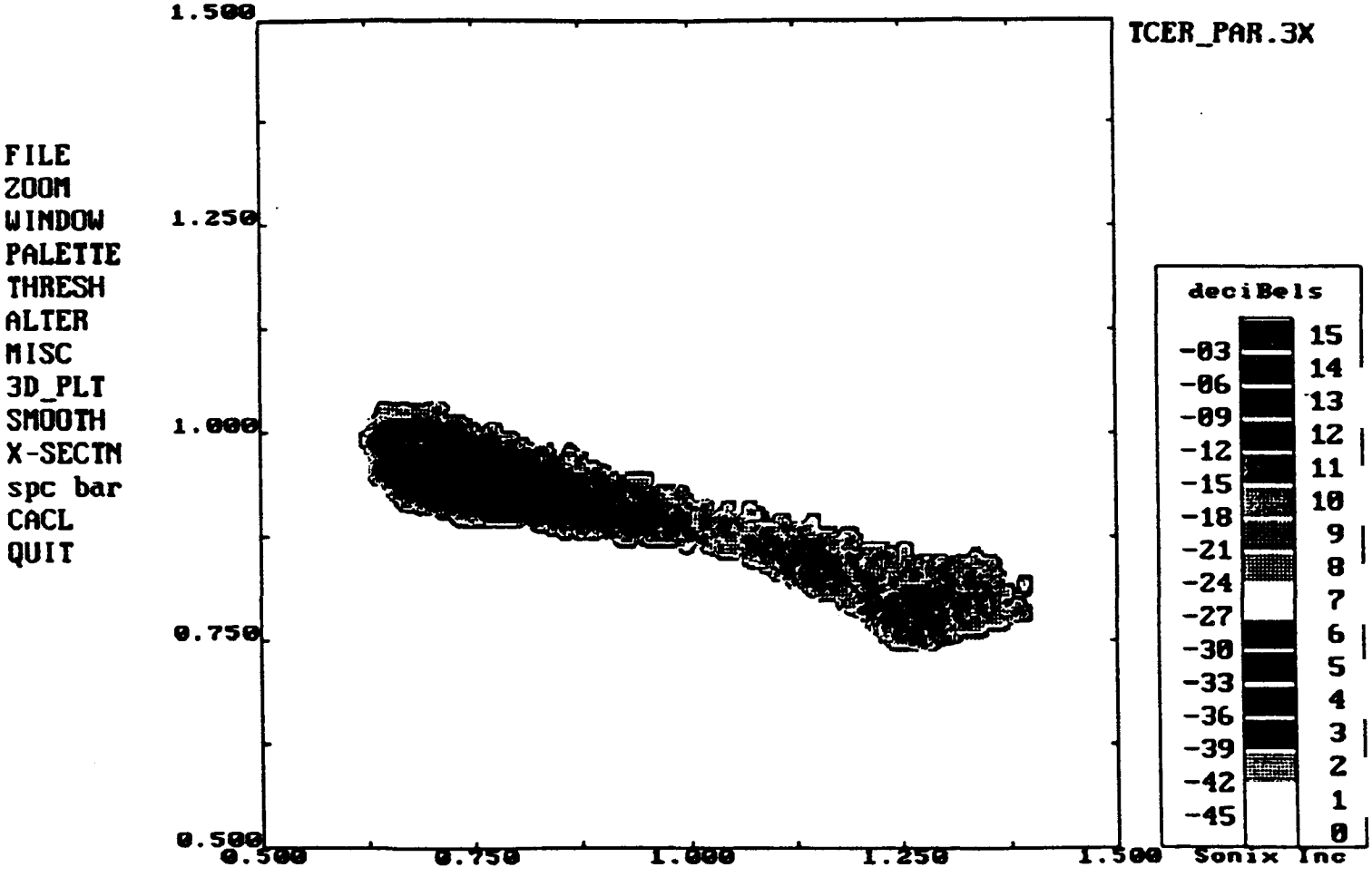


Figure 3. IR thermal image of the surface temperature distribution on a modified SS sample surface during a 1.6 kw YAG laser welding. The surface condition was changed by placing a ceramic particle of 1mm size along the laser path. The right side of the image shows the hot spot caused by the particle.

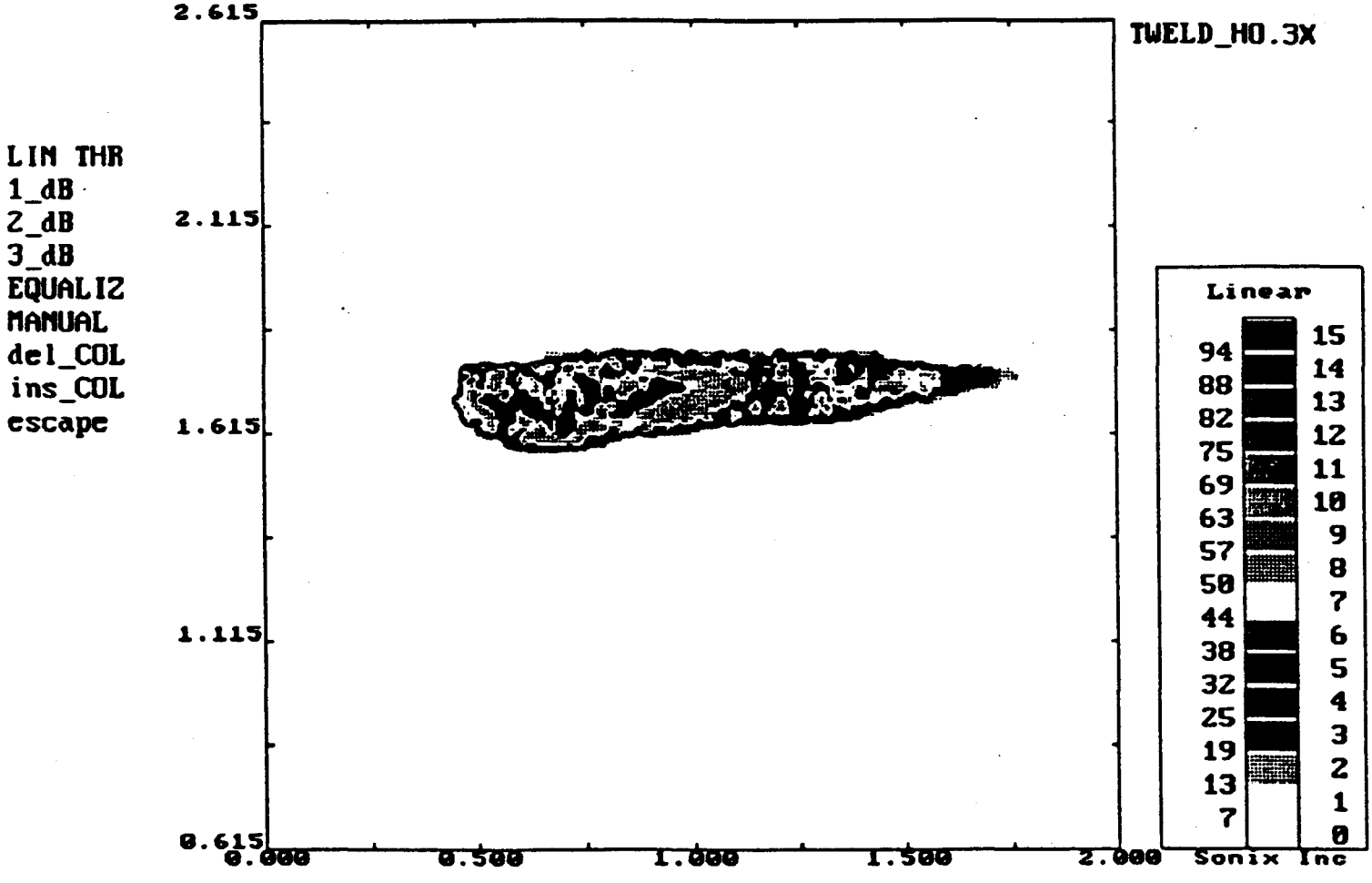


Figure 4. IR image of the surface temperature distribution on a SS sample with a defect during a 1.6 kw YAG laser welding. The defect was simulated by a subsurface hole of 2mm diameter along the laser path. The right side of the image shows the hot spot caused by the hole.

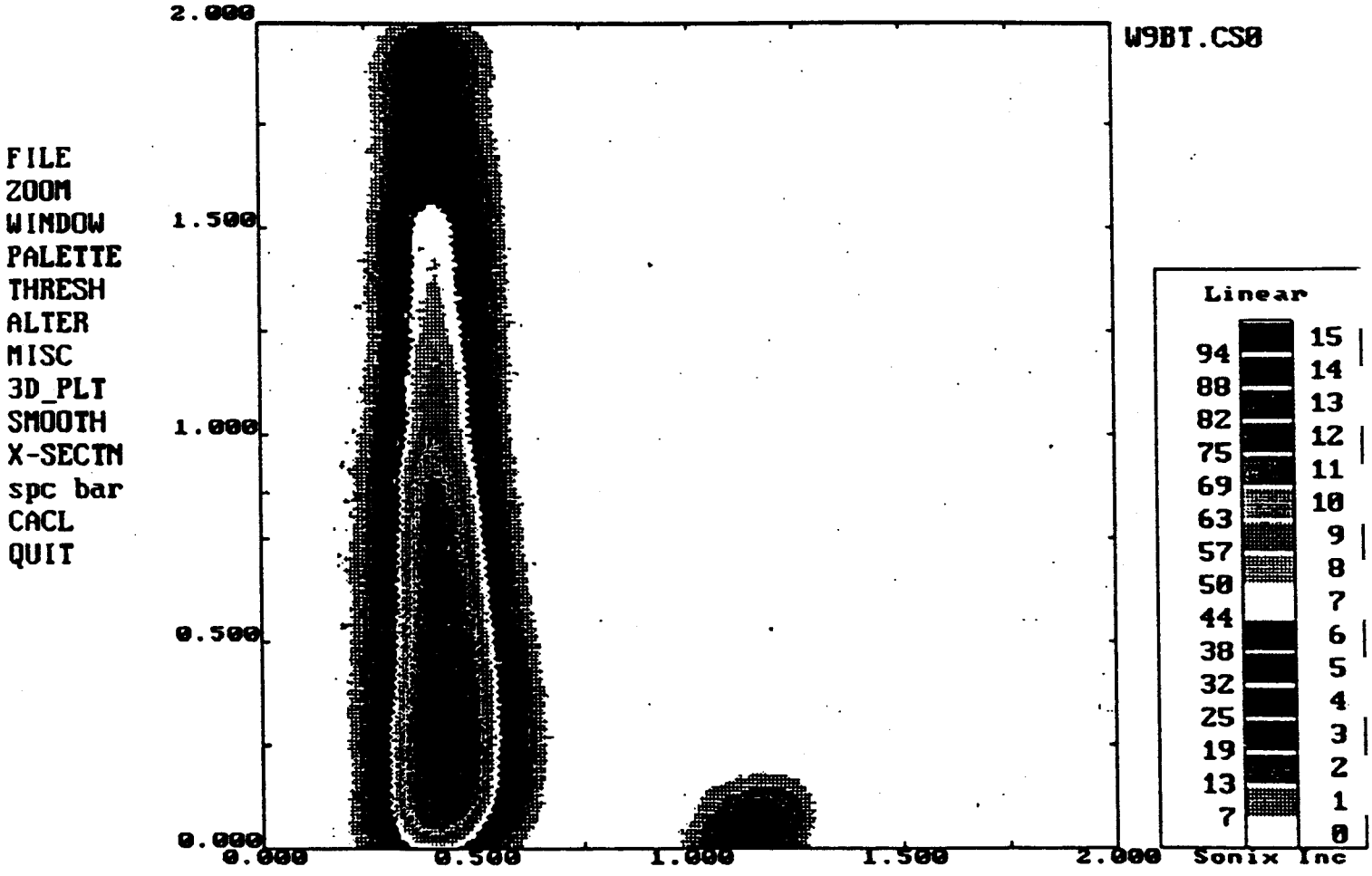


Figure 5. Ultrasonic images of two welds using 1.6 kw YAG laser for welding two 14 gauge stainless steel sheets in a lap welding configuration. The left image indicates a "good" weld between two sheets. The right image indicates no joining except at the edge. These ultrasonic diagnostics were verified by visual inspection of the plates.

91-039R1 -- EXPLORATORY INVESTIGATIONS OF THE TRIBOLOGICAL PROPERTIES OF FULLERENE COMPOUNDS

Associate Laboratory Director Area: Energy, Environmental, and Biological Research

Principal Investigator: G.R. Fenske, Materials & Components Technology

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 28.6K
FY 1992	$ 54K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: The objective of this research was to determine whether or not newly discovered molecular forms of carbon, C_{60} and C_{70}, that have been termed Fullerenes or "buckeyballs", have any potential for improving tribological (friction and wear) properties of advanced engineering materials.

Approach: New molecular forms of carbon were recently discovered. These molecules consist of 60-, 70-, (and more) carbon atoms arranged 3-dimensionally in a form of a soccer ball. They have been nicknamed "buckeyballs" after **Buck**minster Fuller who pioneered geodesic-shaped structures that look similar to soccer balls. Predictions indicate that buckeyball molecules (which are approximately 0.7 -0.8 nm in diameter) can be compressed to a small fraction of their original volume and bounce back to their original volume/structure when the pressure is released. The theoretical predictions indicate that when C_{60} is compressed to one-third of its original height, it is still capable of rolling, thus making it the ideal molecular lubricant.

Conventional liquid lubricants consist of strings or chains of carbon atoms that break up under high shear stresses. In contrast, buckeyballs appear to remain spherical (or in a deformed spherical shape - i.e. a rugby ball) under high stresses and thus might act as extremely small molecular bearings.

Although buckeyballs are predicted to have excellent tribological properties, no experimental research has been performed to prove this hypothesis.

Our approach to this problem was to perform laboratory-scale, pin-on-disc tests to measure the friction and wear of surfaces that have been coated with buckeyballs. The research investigated the effects of applied stress, and sliding distance on the friction and wear coefficients of metallic and ceramic components that were coated with buckeyballs.

Technical Progress and Results: The effort on this program during FY91 focused on assessing environmental, safety, and health considerations of performing tribological tests on fullerene substances, designing/procuring environmental chambers to enclose the pin-on-disc apparatus that were used to test fullerene-coated substrates, modifying a pin-on-disc apparatus

for remote operation in a glovebox enclosure, procurement of fullerene compounds for coating substrates, and procurement of pins and discs for tribological tests.

During FY92, a pin-on-disc tribometer was installed in the environmental chamber and tests were initiated to assess the tribological properties of buckeyball–coated bearing steel. Preliminary tests performed in a dry-nitrogen environment at room temperature using 52100 bearings sliding against hardened 52100 steel discs appear to indicate a thin film of buckeyballs applied to the disc reduced the friction coefficient by a factor of 2 to 3. The thin film of fullerenes also decreased the wear rate of the mating 52100 bearing by approximately one order of magnitude.

Characterization of the morphology of the surfaces of the buckeyball-coated discs suggest that the process used to deposit the films for these tests did not produce a uniform distribution of fullerenes over the disc surface and an effort was initiated to construct an ultrahigh-vacuum thermal-evaporation system to obtain uniform film thicknesses.

Specific Accomplishments: Specific accomplishments for the work sponsored under this project include:

Design and construction of an environmental pin-on-disc tribometer system to permit evaluation of fullerene-coated substrates under controlled environments.

Completion of a preliminary set of friction and wear tests on fullerene-coated bearing steel that demonstrated the lubricious nature of fullerenes.

A patent–disclosure report is currently being prepared based on the results of this work.

The results of this work are being published in Semi-annual progress reports for the DOE-OTM Tribology project.

A paper is currently being prepared for publication in the open literature.

92-179 -- PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION (PECVD)

Associate Laboratory Director Area: Physical Research

Principal Investigators:

D. M. Gruen Chemistry/Materials Science
A. R. Krauss Chemistry

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$ 99K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: The goal of this work is to exploit the tremendous potential for the synthesis of new materials using plasma-enhanced chemical vapor deposition and plasma processing techniques made possible by the use of advanced electron cyclotron resonance plasma sources. These ion sources allow one to have control over a wide range of parameters that influence specific bond-breaking and bond-forming processes within the plasma. In addition, control of substrate bias, plasma gas species, and electron density and temperature within the plasma provide a means of surface modification of the growing film, permitting control of film adhesion, film density, growth mechanism, surface micro-roughness and required substrate temperature for the formation of specific phases. In particular, it is possible to promote the growth of nano-composite materials, i.e. materials which contain inclusions a few nanometers to a few tens of nanometers in size of regions containing either a different morphology, chemical composition, crystalline orientation or crystal structure from that of the matrix material. It is anticipated that this effort will form part of an expanded program at Argonne in the area of engineered materials with controlled and "tailored" nano-structures.

Approach: Control over the number, size, density, composition and shape of nanometer-sized inclusions significantly affects properties ranging from hardness in metals to the current-carrying capacity of superconductors. By using plasma-enhanced CVD, it has been demonstrated previously that the shape of these inclusions can in many cases be controlled to produce e.g. predominantly spherical, disk-shaped, rod-shaped, or layered structures, resulting in materials in which it is possible to control the thermal and electrical conductivity, tensile strength, hardness, transparency, and oxidation resistance.

It is possible to use the computer control available in the new generation of ECR sources to provide both layered structures of dissimilar materials and materials in which composition, matrix density, density of inclusions etc. vary in a continuous manner, thereby forming a continuously graded interface. Layered films can be used as e.g. electronic devices, anti-reflection optical coatings or x-ray optical components. Graded interfaces can be used to provide high thermal shock resistance for e.g. space and fusion materials applications.

Our study involves the establishment of an advanced ECR plasma facility with complete automation of the deposition process and multiple diagnostics for the characterization and

control of plasma parameters. Precise control of the plasma characteristics is particularly important for some of the unique species which we are incorporating in the plasma gas.

Technical Progress and Results: In general, the characteristics of films produced by PECVD are influenced by the gas composition and pressure, substrate bias, and the electron density and temperature of the ECR plasma. Several sets of plasma diagnostics have been designed and are under construction.

A time of flight mass spectrometer to characterize the mass distribution of nano-composites in the ECR plasma has been designed and partially tested utilizing electronically generated input pulses. The mass range of the instrument is from 1 to approximately 1440 amu. The spectrometer inlet system is differentially pumped and designed to sample the gas present in a microwave plasma discharge.

A reciprocating Langmuir probe has been designed to measure electron density and temperature of the plasma. The probe is stepping motor actuated and computer-controlled, and designed to permit sampling of a 4" long chord through the plasma in less than one second, depending on the desired voltage resolution and spatial distance between sampling points.

An optical monochromator has been set up to characterize plasma composition and provide additional information on the plasma excitation process. This system was used on a preliminary basis to characterize the plasma produced by a 2.45 GHz microwave discharge in fullerene vapor, both under vacuum conditions and in flowing helium gas. In order to speed up the data acquisition, a CCD camera and frame grabber have been connected to the data acquisition computer, thereby permitting rapid scanning over a wide wavelength range as well as preselected segments of the spectrum.

Experiments have been carried out on the sublimation and vacuum transport of fullerene vapor, showing that it is possible to repeatedly evaporate and recondense fullerenes at a temperature as low as 350 °C. The effect of a microwave discharge on the fragmentation of fullerene vapor and the consequent ability to maintain the vapor in a microwave discharge is being studied.

Specific Accomplishments: A patent application (ANL-IN-91-27) has been filed on the use of fullerene clusters as a precursor for PECVD diamond film deposition.

92-008 -- SYNCHROTRON RADIATION APPROACHES TOWARD THE FUNDAMENTAL UNDERSTANDING OF HEAVY HYDROCARBON CATALYSIS

Associate Laboratory Director Area: Physical Research (PRA)

Principal Investigator:
K. A. Carrado, Chemistry
P. Thiyagarajan, Chemistry & Pulsed Neutron Source
R. E. Winans, Chemistry

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$ 99K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: The objective of this study is to elucidate structural detail at the molecular level for several systems related to heavy hydrocarbon catalysis, including layered alumino-silicate catalysts and catalyst precursors, petroleum residua, and coal. The approaches used rely on advanced synchrotron X-ray techniques.

Approach: In order to make heavy hydrocarbon catalysis a more viable technology, the interactions between complex organic substrates and catalysts needs to be better understood. The term "heavy" hydrocarbons refers to the large molecules found in petroleum residua and coal. Because of the complexity of these materials, traditional chemical and analytical approaches of characterization have defied resolution of molecular structure, and also their structure-function relationships with catalysts. Therefore, X-ray analysis using bright light sources is exploited to provide insight into the molecular structure of coal and of a suite of specific layered catalysts. These techniques include anomalous small-angle X-ray scattering (ASAXS) and X-ray absorption spectroscopy (XAS).

Technical Progress and Results:

1. XAS of Fe, Ni in coals: X-ray absorption spectroscopy was used to examine the local structure around iron atoms in six of the Argonne Premium coal samples: Wyodak-Anderson (Wyoming), Illinois #6, Pittsburgh #8 (Pennsylvania), Pocahontas #3 (Virginia), Blind Canyon (Utah), and Lewiston-Stockton (West Virginia). While analysis and interpretation of the various spectra is still underway (by S. R. Wasserman of the Chemistry Division), some preliminary conclusions regarding the environment for the iron atoms in these materials can be reached. For those coals which contain substantial quantities of pyrite (Illinois and Pittsburgh), the iron is clearly in a crystalline material. The long range order of the pyrite is reflected in the facile detection of several spheres of coordination for the iron atoms. In

contrast, those coals which do not incorporate significant amounts of iron sulfide appear to have isolated iron atoms. These latter atoms are probably complexed to oxygen, although iron-nitrogen structures may also be present. The Blind Canyon coal, which contains

intermediate amounts of pyrite, apparently contains iron atom in both sulfidic and oxygenic environments.

Samples of both the Wyodak and Illinois coals which had been exposed to air for one year were also analyzed. The Wyodak showed no significant change between fresh and weathered material. This observation is reasonable, since the iron in this coal already exists in an oxygenated form. However, the iron in the Illinois coal undergoes some distinct changes in structure upon weathering. Iron-oxygen type species appear, which is consistent with the oxidation of the sulfur to sulfate.

2. XAS of Metalloporphyrin-Clays: The traditional catalysts of choice for petroleum upgrading are crystalline aluminosilicates called zeolites. Their pore sizes are, however, too small to allow the introduction of the heavy hydrocarbons found in petroleum resids. One class of promising catalytic materials for this application are layered materials, specifically the layered aluminosilicates called clays, because the distance between layers can be almost infinitely varied. A suite of clays containing metalloporphyrins were synthesized with the goal of exploring activity for oxidation catalysis. The focus of the XAS study was the metallation-demetallation behavior of Cu(II)porphyrin-containing samples. For example, XANES and EXAFS of a water-soluble Cu(II)porphyrin both before and after ion-exchange into a clay were observed to be identical. Therefore, copper remains in the macrocyclic ring of the porphyrin upon incorporation into a clay. When XAS was applied to hydrated Cu(II) ion-exchanged into a clay, different and distinctive behavior was noted due to Cu-O versus Cu-N ligation. There remained the question of whether or not a free base porphyrin, upon incorporation into a Cu(II)-containing clay, would complex the Cu(II) ion in the hydrated interlayer region and form the Cu(II) porphyrin macrocycle *in situ*. Some evidence for this occurrence had previously been obtained by UV-visible absorption spectroscopy. Conclusive evidence employing X-ray absorption spectroscopy has now proven that free base porphyrin metallates Cu(II), because the distinctive EXAFS of porphyrin Cu-N ligation was observed.

3. Studies of Layer-Silicate Catalyst Formation: In order to make the preparation of new heterogeneous catalytic materials more precise, systematic and predictable, a wealth of techniques have been applied to probe the mechanisms of catalyst formation. However, much more specific mechanistic detail than is currently available is required, and this is especially true for layer silicate systems. Small-angle neutron scattering (SANS) contrast-variation techniques were exploited to glean mechanistic information from synthetic clay precursor gels. In this study, magnesium hydroxide sol was contrast-matched from the overall scattering profile of a layer-silicate precursor sol for a clay called hectorite. Exchange between hydrogen atoms of $Mg(OH)_2$ and D_2O solvent complicated this, but we have successfully determined that brucite can be contrast-matched with a dispersing medium containing 55% D_2O. The scattering from colloidal silica was also effectively canceled by using 61% D_2O solution. We studied by SANS the clay gel hydrothermally treated for times ranging from 2 to 22 hrs by dispersing them in 55% D_2O. Our calculations have shown that

the scattering length density of the clays formed is equivalent to about 70% D_2O, and hence the clay products should be seen from SANS spectra. Data analysis is currently somewhat hampered by the fact that the flux at the Intense Pulsed Neutron Source during data collection was extremely low, a detriment for observation of the weak contrast-variation scattering. It is also possible that we will have to modify our dialysis procedures in order to insure precise exchange of deuterium.

Specific Accomplishments: This LDRD project supported experiments at the National Synchrotron Light Source and consultations with Dr. Farrel W. Lytle of the EXAFS Co.

Presentations: K. A. Carrado "Surface Chemistry of Clays: Synthesis and Characterization", Amoco Oil Co., Naperville, IL; May 19, 1992.

K. A. Carrado, S. R. Wasserman "X-Ray Absorption Spectroscopy of Copper-Clays", Clay Minerals Society, Minneapolis, MN, November 1992.

92-012 -- CYCLONE Workbench

Principal Investigator: I. T. Foster, Mathematics and Computer Science

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$106.6K
FY 1993	$140K
FY 1994	$100K

Purpose: This project addresses two major computational and numerical challenges that are currently impeding progress in global change research. The first is the use of massively parallels computers to increase model resolution, throughput, and realism. The second is the development of mixed solution and coupled models. To facilitate progress in both areas, we are developing a computational workbench, CYCLONE, that incorporates new mechanisms for coupling models, interpolating data, performing I/O, and managing execution on scalable concurrent computers. This workbench will provide fundamental algorithms and components needed when building geophysical models on parallel computers.

Approach: Research is proceeding in two stages. In the first stage, we are constructing prototype implementations of coupled and mixed-resolution earth systems models, in order to identify the components required in the CYCLONE workbench. We have chosen two modeling systems for this prototyping exercise: a mixed-resolution mesoscale weather model, coupled with a global atmosphere model and a coupled atmosphere-ocean-biosphere model. In the second stage, we will apply the knowledge (and software) obtained in the first stage and construct the CYCLONE workbench.

To provide access to relevant technologies and to accelerate use of results, we have established collaborations with several major research laboratories and companies. We work with the National Center for Atmospheric Research (NCAR) on both mesoscale and global models. We work with the Geophysical Fluid Dynamics Lab on ocean models.

Technical Progress and Results: A prototype parallel implementation of the NCAR/Penn State Mesoscale Model version 4 has been completed. This code is able to exploit up to 16 processors of the Intel Touchstone DELTA computer. Design of a production-quality massively parallel version of Mesoscale Model 5 has been completed. This code allows the creation of nested grids of differing resolutions. Major components of the parallel code have been constructed. This work was reported at the NCAR Mesoscale Model User's Group meeting in October 1992, and will be presented in a paper at the 9th International Conference on Interactive Information and Processing Systems for Meteorology, January 1993.

A specification for a toolkit for constructing coupled earth system models has been completed. This toolkit provides the ability to combine models constructed using different programming systems. A prototype of the software library required to implement this toolkit has been completed; this permits execution of coupled models developed with a dialect of Fortran called Fortran M, on sequential and shared-memory parallel computers.

A prototype of a graphical interface tool has been constructed. This will allow CYCLONE users to control the execution of coupled models in real time.

Specific Accomplishments:

I. Foster and M. Chandy, "Fortran M: A language for modular parallel programming," Preprint MCS-P327-0992, Mathematics and Computer Science Division, Argonne National Laboratory, 1992.

I. Foster and J. Michalakes, "Parallel Implementation of Mesoscale Model version 5," NCAR Mesoscale Model User's Group Meeting, October 22, 1992.

I. Foster, "A Toolkit for Constructing Coupled Earth System Models," Technical Report ANL/MCS-TM-171, mathematics and Computer Science Division, Argonne National Laboratory, October 1992.

I. Foster and J. Michalakes, "Massively Parallel Implementation of the Penn State/NCAR Mesoscale Model," Proc. 9th International Conference on Interactive Information and Processing Systems for Meteorology, AMS, January 1993.

Interactive use of the prototype parallel MM4 code was demonstrated at 1992 SIGGRAPH Computer Graphics Conference, as part of the Showcase exhibit. This featured remote execution of the parallel MM4 on the Intel Touchstone DELTA (located in Pasadena) and simultaneous interactive examination of the results on a graphics workstation in Chicago.

91-038R1 -- VORTEX STRUCTURES IN SUPERCONDUCTORS

Associate Laboratory Director Area: Physical Research

Principal Investigator: P. Plassmann, Mathematics and Computer Science
H. G. Kaper, Mathematics and Computer Science
M. Jones, Mathematics and Computer Science

Funding History:

FY 1990	$ 0K
FY 1991	$ 37K
FY 1992	$170K
FY 1993	$140K
FY 1994	$ 0K

Purpose: In Type-II, layered superconductors, vortex currents around the magnetic flux lines shield the superconducting regions from the effect of the magnetic field, allowing magnetic flux lines to penetrate the bulk of the material. These Type-II superconductors thus have tremendous industrial potential; but, unfortunately, the materials have undesirable physical properties for many applications. This project seeks to develop an understanding of the vortex structure and behavior in Type-II superconductors. It is hoped that such an understanding will enable materials scientists to develop optimum superconductors for high-performance applications.

Approach: The properties of Type-II superconductors have been described phenomenologically by the London theory and the Lawrence-Doniach formulation of layered systems based on the Ginzburg-Landau (GL) equations. However, analytic solutions are known for only a few special cases. Therefore, we are interested in developing computational methods for solving these models.

Our study has involved two approaches: the numerical simulation of the motion of vortices, and the computation of vortex configurations using large-scale optimization techniques on massively parallel computers.

Scientific collaborators were J. Gardner, R. Benedek, S. Shumway, K. Stranburg, and V. Vinokur of the Materials Science Division and G. Leaf, S. Wright, and D. Levine of the Mathematics and Computer Science Division.

Technical Progress and Results: In our numerical simulation studies, we obtained several fundamental results. Using the first approach, we have simulated the planar motion of a single vortex line at moderate temperatures in a random array of point defects; this model is applicable for fields up to approximately 6 T. Using the second approach, we have computed the first three-dimensional equilibrium vortex configurations for layered Type-II superconductors. These computations required the use of a scalable, preconditioned iterative method to obtain efficient processor utilization on the Intel DELTA.

We verified a voltage threshold for vortex motion and found the scaling behavior of the current-voltage curve near the threshold at low temperature. We also directly confirmed the glassy motion of the vortex at moderate temperatures and verified the corresponding glassy exponent.

We have begun an extensive study of columnar defects produced by heavy ion irradiation. Our preliminary results demonstrated hopping of vortices between pinning sites. These results agree with an analytical picture developed in collaboration with
D. Nelson (Harvard).

We have also performed simulations of the Lawrence-Doniach model for simple layered systems in thermodynamic equilibrium. The inclusion of defects and dynamics is the next step in this part of the program.

The Lawrence-Doniach model was also used for our work on massively parallel optimization techniques for computing equilibrium vortex configurations. Using a second-order algorithm based on Newton's method, we have been able to solve complex three-dimensional problems with many vortices. The main computational task in this method is the approximate solution of a sparse linear system. We used a preconditioned iterative method enhanced by a parallel graph coloring heuristic to achieve scalability.

Computational rates of 3.25 gigaflops were obtained on 512 processors on the Intel DELTA. These results represent a hundred-fold improvement over the computation time on a CRAY-2. Thus, our new approach enables us to solve complex three-dimensional problems with many vortices, whereas scientists previously had been limited to two-dimensional problems with very few vortices. The results are especially remarkable because they were obtained with a general-purpose, scalable iterative solver. In addition, the ability to run significantly larger problems on the DELTA allows for the solution of much more accurate three-dimensional superconductor models.

We are currently collaborating with physicists to investigate the phenomenon known as vortex locking. Future work includes modifying the model and discretization so that vortex behavior of more materials can be investigated.

Specific Accomplishments:

J. Garner, M. Spanbauer, R. Benedek, K. J. Strandburg, S. Wright, and P. Plassmann, "Critical fields of Josephson-coupled superconducting multilayers," Physical Review B 45 (1992), 7973-7983.

M. Jones and P. Plassmann, "Solution of large, sparse systems of linear equations in massively parallel applications," Preprint MCS-P313-0692, Argonne National Laboratory, Argonne, Illinois, 1992.

M. Jones, P. Plassmann, and S. Wright, "Parallel algorithms for minimizing the Ginzburg-Landau free energy functional for superconducting materials," Minisymposium, Fourth SIAM Conference on Optimization, Chicago, Illinois, May 1992.

M. Jones, P. Plassmann, and S. Wright, "Parallel algorithms for superconductor modeling," Minisymposium, SIAM 40th Anniversary Meeting, Los Angeles, California, July 1992.

G. K. Leaf, D. M. Levine, J. Rowlan, and V. Vinkur, "Vortex dynamics in high-Tc superconductors," Gordon Conference on Superconductivity, Oxnard, California, January 6, 1992.

M. Jones and P. Plassmann received an honorable mention in the Gordon Moore Grand Challenge Computing Award for their work on "The computation of equilibrium vortex configurations for three-dimensional layered Type-II superconductors." The Board gave this paper, along with three others, special recognition for "high quality."

M. Jones and P. Plassmann received a first prize in the Gordon Bell Prize Competition in 1992, for their paper "Solution of large, sparse systems of linear equations in massively parallel applications." This competition is considered the annual high point of supercomputer research.

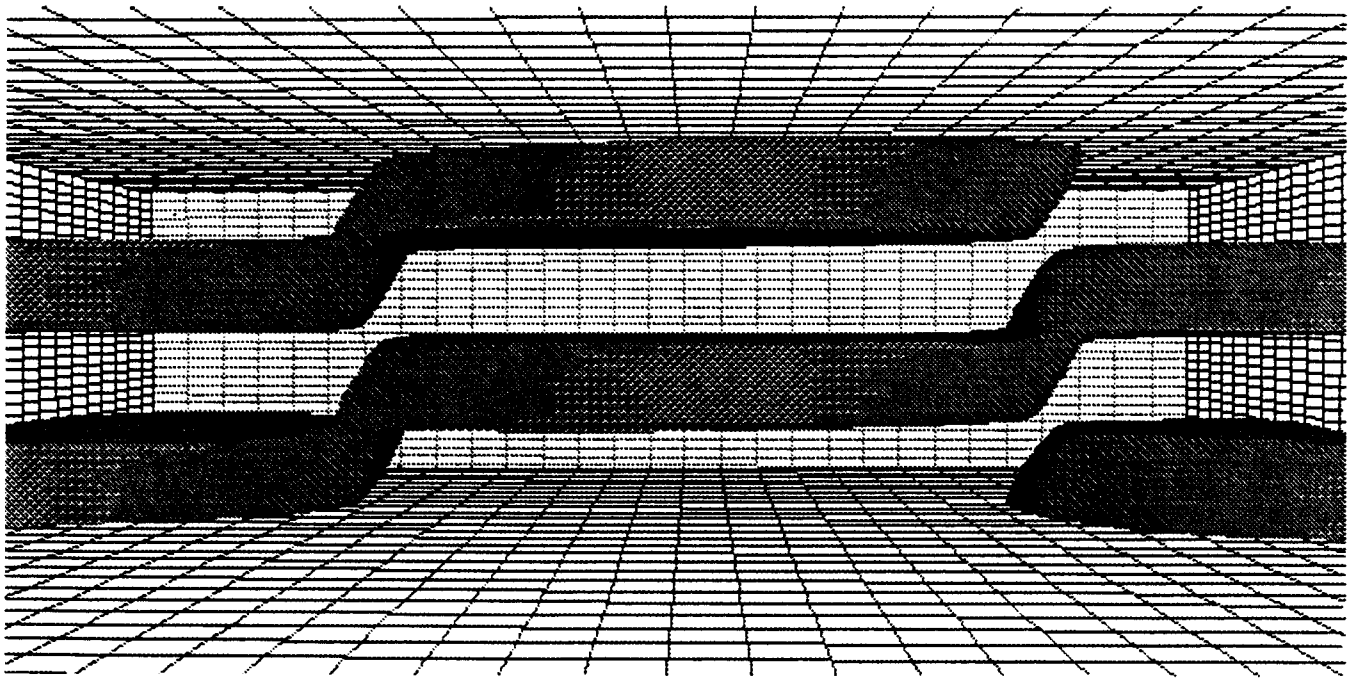


Fig. 1: Equilibrium vortex configuration computed from a three-dimensional phenomenological model of a layered type-II superconductor. Pictured are isosurfaces of the magnetic field strength as the vortices cross superconducting layers. The computations were done on the Intel DELTA and used new optimization algorithms and sparse matrix software developed at Argonne.

91-037R1 -- SCALABILITY ANALYSIS OF "AB INITIO" METHODS

Associate Laboratory Director Area: Physical Research

Principal Investigator: R. Stevens, Mathematics and Computer Science
A. Wagner, Chemistry

Funding History:

FY 1990	$ 0K
FY 1991	$ 32.1K
FY 1992	$147.6K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: To investigate the parallel scalability of *ab initio* quantum chemistry methods, including direct self-consistent field (SCF) Hartree-Fock, configuration interaction (CI), and multi-reference configuration interaction (MRCI) methods on large-scale massively parallel processors (MPP). The main focus is on machines with $O(10^3)$ to $O(10^4)$ processors. Performance models are being developed and used to evaluate the architectural suitability of each method. Our primary goal is to understand and to make predictions about which parallel computational chemistry algorithms are appropriate for various MPP systems. In addition,. our effort is implementing selected methods using portable parallel programming techniques to provide a testbed for benchmark computations.

Approach: This project is exploring innovative scalability analysis techniques for handling dynamic load balancing. New fine-grained parallel decomposition strategies are being examined, and the communications requirements determined. Insights gained from this work are being used to devise prototype implementations for the Touchstone DELTA and other parallel computers and may be used to study dissociation pathways of halogenated aromatics (a difficult set of Grand Challenge problems) and thus used verify the correctness of performance predictions on a number of parallel computers.

The initial focus is on SCF Hartree-Fock methods and CI, MRCI, and multipole methods; but where these methods scale poorly, we shall investigate alternative techniques. For each method, we shall explore parallel data decompositions and determine which can best be used on parallel architectures, including Multiple Instruction Multiple Data (MIMD), and heterogeneous machines. This effort includes identification of the main computational kernels, development of analytical performance models, implementation and validation of the parallel kernels on diverse architectures, and proof of effectiveness on problems involving halogenated aromatics.

A fundamental objective of the DOE High Performance Computing and Communications program is to enable the use of teraflop architectures for the solution of Grand Challenge-class problems, including computational chemistry, within the next few years. This project is intended to help determine what architecture or architectures can be most effectively exploited for computational chemistry applications and to develop the computational techniques necessary to exploit those architectures.

Technical Progress and Results:

Parallel Fock Matrix Construction

A parallel algorithm for Fock matrix construction has been developed. The algorithm distributes the Fock and density matrices over the processors of a massively parallel computer. In the absence of sparsity, the algorithm performs $N^4/8$ two-electron integrals, generates $O(N^3)$ messages, and communicates $O(N^4)$ words of data to construct an N-basis-function Fock matrix on O(N) processors, while requiring only $O(N^2)$ memory. Communication costs can be reduced by an additional factor of J if $O(J\ N^2)$ memory is available. This is considerably better than previously proposed parallel algorithms, which either require $O(N^3)$ memory or perform four times more integral computations. Performance models are used to show that high efficiencies can be achieved on parallel computers if the evaluation cost of a two-electron integral is a constant. Extensions to the algorithm to allow for variable two-electron integral costs and sparsity are currently being investigated.

A prototype parallel code based on ANL-developed simplified Self-Consistent Field testbed has been developed. This is being used to verify the algorithm and to investigate load-balancing strategies. The parallel code is written in the PCN parallel programming language, which provides two benefits: (a) the parallel code can be constructed in a modular fashion, and (b) computation can be automatically overlapped with communication, which is essential if we are to avoid high costs when obtaining Fock values located on remote processors.

Specific Accomplishment:

R. Harrison, "Ab Initio Chemistry in Parallel," Proceedings of First Intel DELTA Applications Workshop, Pasadena, CA, Feb. 1992.

91-036R1 -- PARALLEL MOLECULAR MODELING SYSTEM

Associate Laboratory Director Area: Physical Research

Principal Investigator: R. Stevens, Mathematics and Computer Science
F. Stevens, Biological and Medical Research

Funding History:

FY 1990	$ 0K
FY 1991	$ 31.6K
FY 1992	$159.3K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: To explore the feasibility of using logic-based systems (i.e., automated reasoning and logic programming) to automate the process of x-ray crystallographic structure refinement of biomolecules. To develop massively parallel molecular modeling techniques and to improve visualization of macromolecular systems.

Approach: Many computational problems in molecular biology require modeling and reasoning about constrained systems. A particularly interesting case occurs in the reconstruction of biomolecular structures from x-ray crystallographic data -- a highly labor-intensive process requiring many iterations from a probable guess to numerical simulation to comparison with experimental data and subsequent refinement of the predicted structure. The refinement process is currently one of the most severe bottlenecks preventing a major increase in the number of protein structures solved. With the advent of bright x-ray sources like the APS, this problem will only grow worse.

We have proposed to accelerate the structure refinement process by combining automated reasoning methods and parallel simulation to address the problem of deducing a probable structure subject to certain restraints and constraints. Our intention is to offer the crystallographer a set of tools that will significantly reduce the time currently needed for the reconstruction of biomolecular structures from crystallographic data.

Our approach combines numerical simulation with symbolic computation. Parallel versions of molecular dynamics (MD) models such as AMBER will be used as components in a larger system, a system that will use MD when needed and will also apply to the unknown structure rules of bond angles, conserved structures, and similarities to known structures. The use of a symbolic or reasoning program to set up and run parallel numerical simulations and then apply or disregard the results to the refinement of the unknown structure is a novel feature of our approach.

Technical Progress and Results:

Progress was made in three areas during FY92.

Automated systems for structure determination and analysis - A prototype system has been built for the analysis of x-ray crystallographic structure data. This system, based on logic programming and automated reasoning techniques, incorporates knowledge of allowable protein structure factors and provides a cooperative question-answering capability to explain to the user the steps involved in reaching a particular conclusion. This system is designed to partially automate the determination of molecular structure from three-dimensional electron density data. Its key features include the ability to easily input new structure constraints (rules that must be followed if the protein structure is real) and to handle "tends-to-be" rules that capture human intuition regarding likely properties that a correct protein structure should have. For example, bond lengths in the main chain and dihedral angles between planar groups can easily be computed from existing structures in the protein database, and this data can be used to derive the "rules" for the system to apply to an unknown structure. The system is also being designed to automatically "discover" the conformation of a protein by fitting the backbone and sidechains into the electron density. This feature requires the ability to recognize the most likely "signatures" in the density that correspond to a particular residue. Development of the prototype automated system for structure determination is continuing under support from DOE.

Parallel molecular dynamics methods - Efforts in FY92 have focused on the development of massively parallel implementations of classical molecular dynamics simulations. Our approach has focused on two large-scale modeling systems and a third system for prototyping. The basic goal of this project is to develop "scalable" parallel implementations of AMBER and XPLOR. Existing parallel implementations developed elsewhere are limited in the size of the problem by the fact that coordinate data is duplicated on each node in the parallel computer. Also, existing systems do not perform well when the number of processors is close to the number of atoms in the system (i.e., they are coarse grained, requiring on the order of 100 atoms per processor to achieve acceptable parallel efficiencies). We are attacking the problem from two angles. First, we are evaluating fine-grained parallelism using the language system PCN developed at ANL and Caltech. Second, we are focusing on algorithms that are likely to give good performance when the number of atoms and number of processors are approximately equal. The PCN system has support for fine-grained algorithms and is being used as a prototyping and development environment. This project is evaluating the performance of PCN's merger, distributor, and virtual topology/port constructs for data communication and distribution. Parallel implementations are in progress and will be tested using the Intel Touchstone DELTA and parallel computers from IBM.

Visualization of molecular models using virtual reality techniques - In FY92 this project was involved in development of the Cave Automated Virtual Environment (CAVE) virtual reality display system. In this system four 10' x 10' projection display screens were used to build a walk-in room that provides a three-dimensional environment for the display of scientific data. In particular, this system has been used to display static three-dimensional and animated sequences of molecular structures.

Specific Accomplishments:

C. Cruz-Neira et al., "The CAVE: Automatic Virtual Environment," Communications of the ACM **35**, no. 6 (June 1992.)

F. Stevens and R. Stevens, "Protein-Protein Interactions Kinetics," Proceedings of the First Intel DELTA Applications Workshop, February 1992.

R. Stevens, "Computational Science Experiences on the Intel Touchstone DELTA," COMPCON, 1992.

92-016 -- PARALLEL MONTE CARLO METHODS FOR REACTOR MODELING

Associate Laboratory Director Area: Physical Research

Principal Investigators: D. Malon, Computing and Telecommunications
R. Blomquist, Reactor Analysis
T. Canfield, Computing and Telecommunications

Funding Profile:

FY 1990	$ 0
FY 1991	$ 0
FY 1992	$101.9K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: The aim of this project is to explore and develop the underlying computational technologies necessary to enable full-core Monte Carlo depletion modeling of nuclear reactors. High-performance parallel algorithmic methods appropriate for reactor analysis computations must be developed in order for such modeling to become feasible. The detailed modeling capabilities for which this project provides a foundation are expected to produce significant economic benefits for the American nuclear power industry and its customers, and to bolster the Laboratory's position to combine its separate strengths in reactor analysis and high-performance computing to serve as a national resource for computational nuclear power analysis.

Approach: Extrapolations based upon smaller simulations predict that full-core Monte Carlo depletion simulations of nuclear reactors would require on the order of 1,000,000 hours of CRAY X-MP/14 computer time. The pace of progress in the computing industry suggests that such computations, long an impossible dream of reactor analysts, can become feasible in the next several years, but only if the power of massively parallel computing and advanced algorithmic methods can be brought to bear on the problem. Success will require close collaboration among reactor analysts and computational scientists.

The scope of this project is investigation and development of computational methods that will provide the underlying technology for these numerical simulations of Grand Challenge magnitude. Our approach is three-pronged. It encompasses exploration of methods to parallelize Monte Carlo neutronics techniques currently in use by reactor analysts, theoretical and empirical analyses of flux eigensystem biases, and involvement of commercial nuclear power providers in the development program. Such industry involvement from the earliest stages is important; it ensures the relevance of this work to commercial problems, refines our focus, and guarantees the transfer of technology to the private sector.

Technical Progress and Results: We have inaugurated specific collaborations with the nuclear power industry. Staff engineers Del Pallotta of Commonwealth Edison and Steve Rowe of Illinois Power are visiting Argonne on a regular basis and, in conjunction with project staff, have undertaken efforts to apply Argonne computational technology to problems of interest to commercial nuclear utilities. Results of the Commonwealth Edison collaboration to date include determination of isotope cross-sections (based on Evaluated Nuclear Data File data) at 300 and

1000 degrees Kelvin, geometric layout of two different pin bundle designs (Figure 1), and computational comparisons between results produced by the Argonne VIM neutronics code and those of the CASMO package used internally by Commonwealth Edison. Among the quantities of interest in these studies are fuel bundle reactivities and comparisons of individual pin powers within bundles. The Illinois Power collaboration is in an earlier phase and has involved development of isotope cross-section data at vendor-recommended operating temperatures for use in subsequent neutronics calculations.

We have developed a parallel code that finds principal eigenvalues and eigenvectors in weighted Markov chain problems by Monte Carlo methods, and analyzes biases compared with deterministic (power method) computations. (These comparisons are possible because the transition matrices are known; in reactor analysis problems, transition probabilities can only be estimated via simulation.) The code runs on a variety of platforms, including the Intel Touchstone DELTA, and will be useful in efforts to model and understand biases arising in neutronics eigenvalue computations. We have in tandem. begun corresponding theoretical bias analyses.

We have undertaken parallelization of Monte Carlo neutronics simulations. We have analyzed data dependencies and control structures in the VIM neutronics package, and have developed a coarse-grained parallelization strategy. We have revised VIM's particle-banking data structure for parallelization by history, and have addressed (possibly memory-size-dependent) energy banding issues. We have implemented a parallel random number generation strategy that accommodates the Monte Carlo Neutronics Package (MCNP) generator; our current generator ensures parallel reproducibility by straightforward skip-ahead methods.

Ongoing efforts address development and implementation of paralles methods to accommodate or circumvent VIM's dynamic memory management scheme.

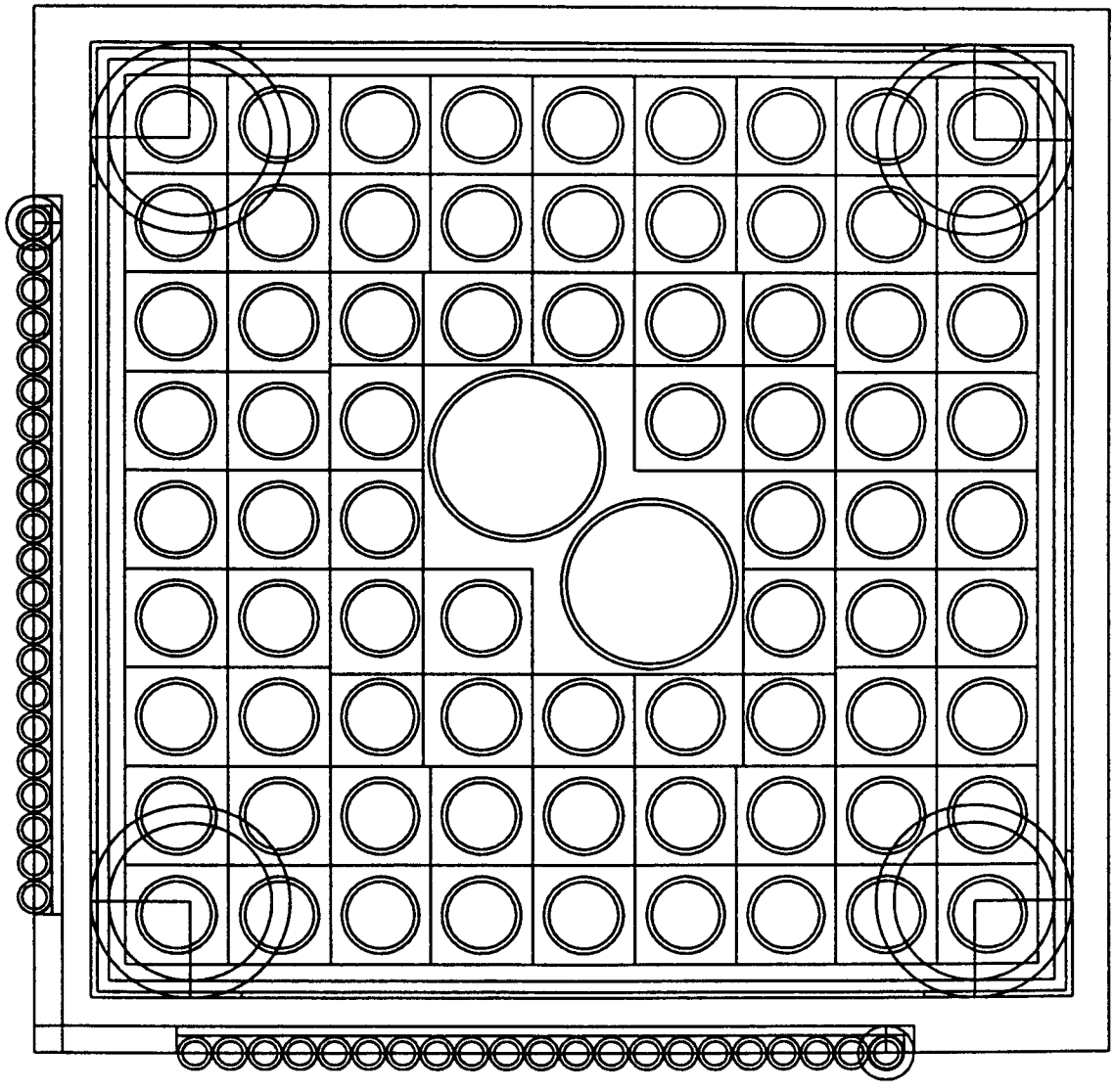
This initiative has spawned a number of related proposals for larger-scale programs for which this work provides a foundation. These proposals include the following:

- *Full-Core Monte Carlo Depletion Simulations of Nuclear Reactor*, submitted as a Grand Challenge computational science component of the Argonne, Commonwealth Edison, the Electric Power Research Institute, Illinois Power, the National Center for Supercomputing Applications, Northwestern University, the University of Michigan, and the University of Illinois at Urbana-Champaign.

- *State of the Art Parallel Monte Carlo Methods with Applications to Nuclear Reactors Modeling*, latest revision June 1992, submitted to the Electric Power Research Institute.

- *Nuclear Power Analysis Center*, currently under development. Collaborators include those participating in the *Full-Core* proposal, and the Massachusetts Institute of Technology, Purdue University, and the University of Wisconsin.

GE11 Controlled BWR Pin Bundle



92-109 -- CRYSTALLOGRAPHIC DATA PROCESSING SOFTWARE DEVELOPMENT FOR SYNCHROTRON APPLICATIONS

Associate Laboratory Director Area: Energy, Environmental, and Biological Research

Principal Investigator: E. M. Westbrook, Biological and Medical Research

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$298.4K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: To develop the next generation of data processing software that optimizes the utilization of high brilliance x-ray sources for protein crystallography.

Approach: Fast and accurate data collection for protein crystallography requires the use of specialized area-sensitive detectors with attributes and characteristics which transcend those of laboratory-based designs. Such superior detectors, however, strain the capabilities of existing computing hardware and software, creating a data through-put bottleneck that limits the efficiency and productivity of synchrotron beamlines as effectively as any deficiency in x-ray optics might.

A third generation Argonne CCD-based area detector is being designed and developed for protein crystallographic research by ANL. Although the hardware was developed, no one was exploring the exciting new conceptual software areas to harness the potential of the CCD detectors.

Under support from this LDRD project, Dr. J. Pflugrath (Max Planck Institute, Martinsried, Germany) has initiated major modifications and improvements of computer software analysis to conform to the realities of state of the art synchrotron data-collection environments.

Technical Progress and Results: During fiscal year 1992, this research and development of the software has greatly expanded and enhanced the potentials of CCD detector work for protein crystallography. Capabilities were introduced into programs that were never before previously available. Laue diffraction data processing and multiple-energy anomalous dispersion (MAD) phasing are now possible at higher resolutions. Data processing speed was increased dramatically.

Specific Accomplishments:

1. Two types of programs to expand the current state of research in this area were explored. One set concentrated on work for all VMS architectures, the other concentrated on all UNIX architectures.

2. Success was achieved in writing codes that correct images for dark current and incident beam intensity variations. Acceleration of code was also achieved, making the overall rate of data processing faster than data collection: For example, in one test case it took 59.5 minutes

elapsed time (17.4 minutes exposure time) to record 310 image frames, representing 62° of crystal rotation. The same data was processed in 21.5 minutes elapsed time (14.8 minutes CPU time) by enhanced software developed under this program.

3. To test the new methodologies, data was collected, processed, and analyzed from two crystals being studied at Cold Spring Harbor Laboratory. The T7 phage lysozume and S100b restriction enzyme were used.

4. New capabilities of the software were then tried on Laue diffraction methods. This was done by installing software on the X26C Laue beam line at Brookhaven National Laboratory.

5. Processing code was originally written for a Convex computer. The new methodologies were incorporated in the Convex framework which initially caused problems. The problems were corrected and everything appears to be working in our environment.

6. Software routines were modified, and a distributed processing methodology was installed on the NSLS Structural Biology Center (SBC) computers. X- Windows programs were obtained from John Campbell of Daresbury Laboratory and Phil Evans of the Medical Research Council, and have been modified to work on several platforms. File-sharing capabilities have now been installed on SBC computer platforms using appropriate protocols. All SBC computers can now share data files.

91-012R1 -- HUMAN GENOME SEQUENCING BY HYBRIDIZATION

Associate Laboratory Director Area: Energy, Environmental, and Biological Research

Principal Investigators: R. Drmanac, Biological and Medical Research
R. Crkvenjakov, Biological and Medical Research

Funding Profile:

FY 1990	$ 0K
FY 1991	$300.1K
FY 1992	$267K
FY 1993	$ 95K
FY 1994	$ 0K

Purpose: The aim of this proposal is to provide necessary support for the sequencing by hybridization project of the Human Genome Initiative by aiding its establishment in ANL and providing funds for the methodological development of this technology towords miniaturized arrays of samples. The effort at miniaturization of sequencing by hybridization (SBH) will ultimately explore an original approach to making nucleic-acid-bound matrixes using microbeads as obligatory intermediates.

Approach: The human genome sequencing effort is proceeding through both the evolution of conventional techniques and the development of novel methods. The former is based on the classical techniques of Sanger and of Maxam and Gilbert, which are rate-limited by a lengthy fractionation step and the labor-intensive process of sequencing longer DNA fragments. In contrast, novel methods promise to provide sequence data at much higher rates. A novel method pioneered by the co-PIs is sequencing by hybridization. This is the only new method that has successfully passed a proof-of-concept test. This method does not have a fractionation step; rather, the sequence data are accessed within recombinant DNA clones by hybridization with short DNA oligomers. The current success depends fundamentally on algorithms for the assembly of extended DNA sequences from the oligomer content of the clones and in methods for efficiently acquiring oligomer data. Much of the further development in SBH will involve automating the biochemistry, mechanical processing, and data capture.

One way of implementing this technique includes extensive miniaturization, with data readout by fluorescence microscopy from matrix-bound oligomers able to capture fragmented DNA from a clone. Such development offers the advantages of simultaneous reactions of synthesis or binding of nucleic acid to physically or chemically different beads, potentially allowing economical production of matrixes of significantly higher complexity. The hybridization capture at the matrix position of a known oligomer will confirm the presence of a corresponding sequence in the clone, providing all the oligomer information on a single clone simultaneously. Arrays with longer unit oligomers will allow interrogation of larger clones, with a concomitant decrease in the size of the libraries that must be prepared.

Satisfactory discrimination so far has not been obtained with oligonucleotides attached to a support. Besides excluding or limiting the negative influence of steric factors on hybrid formation, there is a chance to improve discrimination with bound oligonucleotides if a more

systematic and thorough effort to understand sequence- and context-dependent effects in short oligomer hybridization is made. Technologically, the bound- oligonucleotide approach becomes more important if longer oligonucleotides are used.

Technical Progress and Results: Fiscal year 1991 was devoted to bringing the SBH research group to ANL and to establishing a productive laboratory. This was accomplished in less than eight months. In FY 1992, results were obtained that demonstrate the power of the SBH method. A decision was made to test the limits of mechanical miniaturization first. This can give an immediate payoff in the implementation of SBH for analysis of real biological samples such as 100,000 genes. Also, isotope ^{33}P is now available (about 60 μm resolution in comparison to 300 μm for ^{32}P); in addition, this isotope is safer to work with. It brings mechanical miniaturization close to the capabilities of physicochemically more complicated technology based on the microbeads. We did not succeed in some attempts to attach DNA to glass modified by amino-propyltriethoxysilane and oligonucleotides to Sepharose 4B modified by 6-aminohexanoic acid/n-hydroxysuccinimide. However, a significant advance in miniaturization of the DNA array was accomplished by robotic spotting on nylon membranes using a metal pin array: clone sample density was increased from 10 to 144 per cm^2 with a potential of 324 samples. To achieve this density, we modified the tablet and software of the robotic station Biomek1000 and designed special stainless steel pins, 0.3 mm in diameter. To be able to analyze a dense array of samples close to the limit of resolution for ^{33}P, we have developed image analysis software to correct for mechanical imprecisions in spotting. In the course of the work, we realized that by increasing the density of oligonucleotides per surface and applying long genomic DNA, the background due to the complexity of the DNA will also increase. We have proposed a solution that is based on a combination of oligonucleotides attached to the surface and labeled oligonucleotides applied in solution. A ligation step is included to join oligonucleotides from the solution when hybridized back to back with attached oligonucleotides. In this scheme there is no labeling of complex genomic DNA and consequently the background will be very small. By synthesis of two sets of 6-mers (8,000 probes), the content of 12-mers (16 million) can be determined. This represents a basis from which an investigation of the further SBH miniaturization by robotic spotting by pin array and, eventually by using microbeads, can be profitably explored in fiscal year 1993.

Specific Accomplishments: Upon external review, funding for the implementation of the present level of the achieved miniaturization for cataloging genes and ultrafine genomic maps has been obtained from DOE on a continuing basis. The FY 1992 work resulted in two invention disclosures, three publications, two papers submitted, and one paper in preparation. The co-PIs gave eight invited presentations at international genome meetings and presented several seminars at research institutions throughout the country. Tasks not covered by DOE follow-on funding will be pursued under LDRD in FY 1993.

Publications:

"Sequencing by oligonucleotide hybridization: a promising framework in decoding of the genome program?" Drmanac, R., Labat, I., Strezoska, Z., Paunesku, T., Radosavljević, D., Drmanac, S., and Crkvenjakov, R., in Proceedings of the First International Conference on Electrophoresis, Supercomputing and the Human Genome, ed. by C. R. Cantor and H. A. Lim (World Scientific Publishing Co., Singapore, 1991) pp. 47 - 59.

"Sequencing by hybridization (SBH) with Oligonucleotide Probes as an Integral Approach for the Analysis of Complex Genomes," Drmanac, R., Crkvenjakov, R., Int. J. Genome Res., 1 (1992) 59 - 80.

"Sequencing by hybridization: towards an automated sequencing of one million M13 clones arrayed on membranes," Drmanac, R., Drmanac, S., Labat, I., Crkvenjakov, R., Vicentic, A., and Gemmell, A. Electrophoresis, 13 (1992) 566 - 573.

92-108 -- STRUCTURAL BIOLOGY AND THE HUMAN GENOME: CRYSTAL STRUCTURES OF DNA COMPLEXES

Associate Laboratory Director Area: Energy, Environmental, and Biological Research

Principal Investigator: E. M. Westbrook, Biological and Medical Research

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$242.1K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: The main goal of this project is to study the structure of biologically important protein-nucleic acid complexes (DNA and RNA) in humans and other eukaryotes, in order to better understand how proteins interact with nucleic acids, and the roles such interactions play in the regulation of cellular processes.

Approach: The explicit results of each project in macromolecular crystallography are the coordinates for the thousands of atoms that make up the structure of that macromolecule. Such information is of great value in understanding the function of that molecule, and its role in the biochemistry and genetics of an organism. However the crystallographer cannot work in a vacuum: he must coordinate with biochemists and molecular biologists who study metabolism, genetic regulation, and other activities. These collaborators must identify important subjects for crystallographic analysis, isolate and purify proteins or genes pertinent to such subjects, amplify genes, express them, and deliver to the crystallographer a sample that can be successfully crystallized.

The main goal of this project is to study the structure of biologically important protein-nucleic acid complexes (DNA and RNA) in humans and other eukaryotes, in order to better understand how proteins interact with nucleic acids, and the roles such interactions play in the regulation of cellular processes. This required the identification of research subjects, particularly the aggregation between proteins and nucleic acids. Proteins had to be produced, isolated, and crystallized.

Technical Progress and Results: Many of these projects are centered upon aggregation between a protein and a fragment of nucleic acid. Such aggregation states are particularly important in molecular biology, since proteins regulate genetic expression through direct and indirect contact with DNA and RNA. Unfortunately such aggregates are also among the most difficult macromolecules to crystallize successfully, since one must use technologies that are compatible with both protein and nucleic acids, and the binding forces between these divergent components tend to be subtle. The research group worked very hard on identifying the proteins that would be best suited to this analysis and determining the parameters for growth of the crystals using these proteins.

1. Success was achieved in producing and purifying a bacterial cyanase. Crystal growing parameters were determined and crystals of cyanase have been grown. They appear to be large enough and sufficiently well ordered that their structure determination can begin. Explicit collaborations have been set up with outside molecular biologists and protein chemists so that supplies of these various proteins and complexes can be obtained. This is a very important enzyme in environmental remediation areas. The bacteria in layman's terms chews up or degrades the hazardous material cyanide. Determining the structure of this material could significantly improve the techniques for handling and disposing of this material.

2. The team was not yet successful in growing the aminoacyl-tRNA synthetase, bound with cognate tRNA.

3. Heat shock factor protein (HSF), complexed with its DNA target was successfully grown and the parameters for growth were determined.

4. The DNA binding domain of testis-determining factor, complexed with DNA target was experimented with and the experiments determined that the parameters for crystallization could not be pinned down. Crystallization attempts should continue.

5. Chaperone proteins from thermophilic bacteria were successfully crystallized. These proteins are important in making the protein fold correctly. The ribosomal protein S4, complexed with its RNA target was successfully crystallized.

A Field Work Proposal (FWP) has been funded by the DOE/Office of Health and Environmental Research. Work will begin in January, 1993 which follows up on these accomplishments.

92-113 -- NEW MASS SPECTROMETRY APPROACHES FOR DNA SEQUENCING

Associate Laboratory Director Area: Energy, Environmental, and Biological Research

Principal Investigator: Jerry E. Hunt, Chemistry
Randall E. Winans, Chemistry

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$110.1K
FY 1993	$ 85K
FY 1994	$

Purpose: This new initiative seeks a method for faster sequencing of DNA. The approach relies on mass spectrometry to directly analyze DNA fragments.

Approach: Sequencing currently involves cloning a fragment of DNA, running it through four base identifying reactions, separating the pieces from each reaction by gel electrophoresis, then reading each piece to determine the sequence. This a very slow, tedious and expensive process. The use of mass spectrometers in place of gels would be a high-speed alternative to sequencing that would have applications to the human genome project.

Our approach addresses methods for the direct, successive analysis of the four base identifying reactions by mass spectrometry. This provides the mass of each oligonucleotide terminating in each of the base residues. The sequence is inferred by the increments in mass calibrated on an absolute mass scale.

The main objective is to volatilize and ionize DNA fragments. We bring our full mass spectrometry arsenal to bear on this problem. We use the more mature methodologies of FAB (Fast Atom Bombardment) mass spectrometry, ^{252}Cf-PDMS (Plasma Desorption Mass Spectrometry), and tandem mass spectrometry to establish sequences for smaller oligonucleotides. The newer techniques of laser desorption and laser multiphotoionization mass spectrometry, which are in place in our lab, were developed for higher molecular weight DNA residues. Laser desorption, either from a matrix or from a neat sample, is relatively straightforward and is in use to analyze large biopolymers (e.g., proteins with molecular weights of up to 150,000), additives in polymers, and other organic compounds. We have also demonstrated that selective ionization of desorbed material without fragmentation can be accomplished in a postionization step.

Technical Progress and Results: One of the hurdles to be overcome is volatilization and ionization of the DNA fragment. Improvements in mass spectrometric techniques have resulted in routine extension of the mass range beyond 5000 amu. We have a wide variety of mass spectrometric techniques in our laboratory that we have used for nucleotide analysis. Our first goal was to study the behavior of small nucleotide fragments in mass spectrometric techniques other than Matrix-Assisted Laser Desorption/Ionization (MALDI) to gain insight into the production of molecular ions and the fragmentation behavior of gas-phase nucleotide ions. We have used tandem FAB MS in a 4-sector instrument to investigate simple fully protected

dinucleotides; an example, d(GpCp), is shown in Figure 1. The sample was run in a 3-nitrobenzyl alcohol matrix. Tandem mass spectrometry relies on selection of parent molecular ions by one stage of mass analysis and their subsequent fragmentation and analysis of sequence-specific product ions by a second mass analyzer. To date tandem mass spectrometry of nucleotides has not been extensively explored. Figure 1A shows the molecular ion $(M+H)^+$ at 1406 and a fragment ion of the 4,4'-dimethoxytrityl (DMT) protecting group at m/z 303.3. Figure 1B shows a structurally significant fragmentation ion at m/z 766.3. This intense ion corresponds to cytosine residue with its attached protecting groups. No fragment of the 5'-DMT blocked guanine containing residue is present. The other weaker fragment ions in the spectrum are related to combinations of losses of protecting groups (-Cl, $-CH_2CH_2CN$, $-COC_6H_5$, -DMT etc.) from the molecular ion or fragment ion. The FAB MS study provides two pieces of information. One, molecular ion species of nucleotides can be produced. Two, sequence-specific information may be inferred from fragmentation ions. Similar results were obtained from another ionization method, ^{252}Cf-PDMS using time-of-flight (TOF) analysis, although matrix effects, most notably addition of Na^+ or K^+ (cationization) complicated the spectrum. These last experiments were successful. They provide a basis for gas-phase ion production, behavior, and analysis of simple nucleotides. From this result we can reasonably anticipate similar gas-phase behavior in the MALDI spectra.

A first step in MALDI was to produce positive and negative TOF spectra of bovine insulin, molecular weight 5733. Figure 2 is the positive ion mass spectrum of a caffeic acid matrix/insulin sample generated by 30 shots of a 337 nm nitrogen laser desorption. For calibration accuracy a small molecular weight peptide, luteinizing hormone releasing hormone (LHRH) (MW 1182) was added to the sample (see Figure 4). Clearly visible are the molecular ion of insulin, the LHRH spike and an insulin dimer ion of molecular weight 11466. The mass resolution at m/z 5733 in this spectrum is 200. Polynucleotide fragments in the mass region of 12000 would correspond to approximately 40-bases, a useful mass range for the proposed sequencing method.

We obtained 10 samples of oligodeoxynucleotide 10-mers from R. Crkvenjakov and examined them all. The 10-mers have each of the four bases at either end of the chain, in other words, the inner 8 bases are capped with A, T, C, or G on the 5' and 3' ends. Using 337 nm radiation and 3,5-dinitrobenzoic acid as a matrix we have successfully detected negative molecular ions of this range of base compositions of oligo–deoxynucleotide 10-mers. Figure 3 shows the remarkably strong ion signal obtained for the singly-charged parent molecules. This spectrum is a sum of 50 laser shots at a repetition rate of 10Hz, i.e., 5 seconds. The total time from sample preparation, laser alignment and focusing to completion of the acquisition was 20 minutes. This time is a factor of 10 shorter than gel techniques. This could be shortened considerably in routine analysis. The resolution was less than that achieved for proteins, although the maximum in the peak corresponded well to the actual average mass of the 10-mers. The mixture of compounds would be expected to generate a peak over 80 mass units wide. A factor affecting the resolution is the wavelength of the laser. The nucleotides bases absorb strongly at 337 nm. The observed peak shape results from metastability, i.e., coupling energy directly into the oligodeoxynucleotide. In general, the best results for matrix assisted desorption are obtained for wavelengths where the sample only weakly and the matrix absorbs strongly. The success with 337 nm radiation is therefore very surprising and encouraging. The molecular weight of the average of the 16 possible sequence combinations of this sample is 3009.5. To fully resolve the molecular ions in

this sample a resolution of better than 1 part in 3000 is needed. For a low resolution mass spectrum (as here) the mass distribution alone without isotopic contributions corresponds to a single peak that is 80 mass units wide. Other 10-mer sequences show similar mass spectra. A good indication that the 10-mers are absorbing energy and fragmenting is the presence of strong fragment ion signals of all the nucleotide bases at low mass. Wavelength and matrix variations can reasonably be expected to ameliorate this complication and improve the ion yield as well as the quality of the spectrum.

Specific Accomplishments:

A pre-proposal for DOE OHER funding has been submitted as a result of initial experimental success.

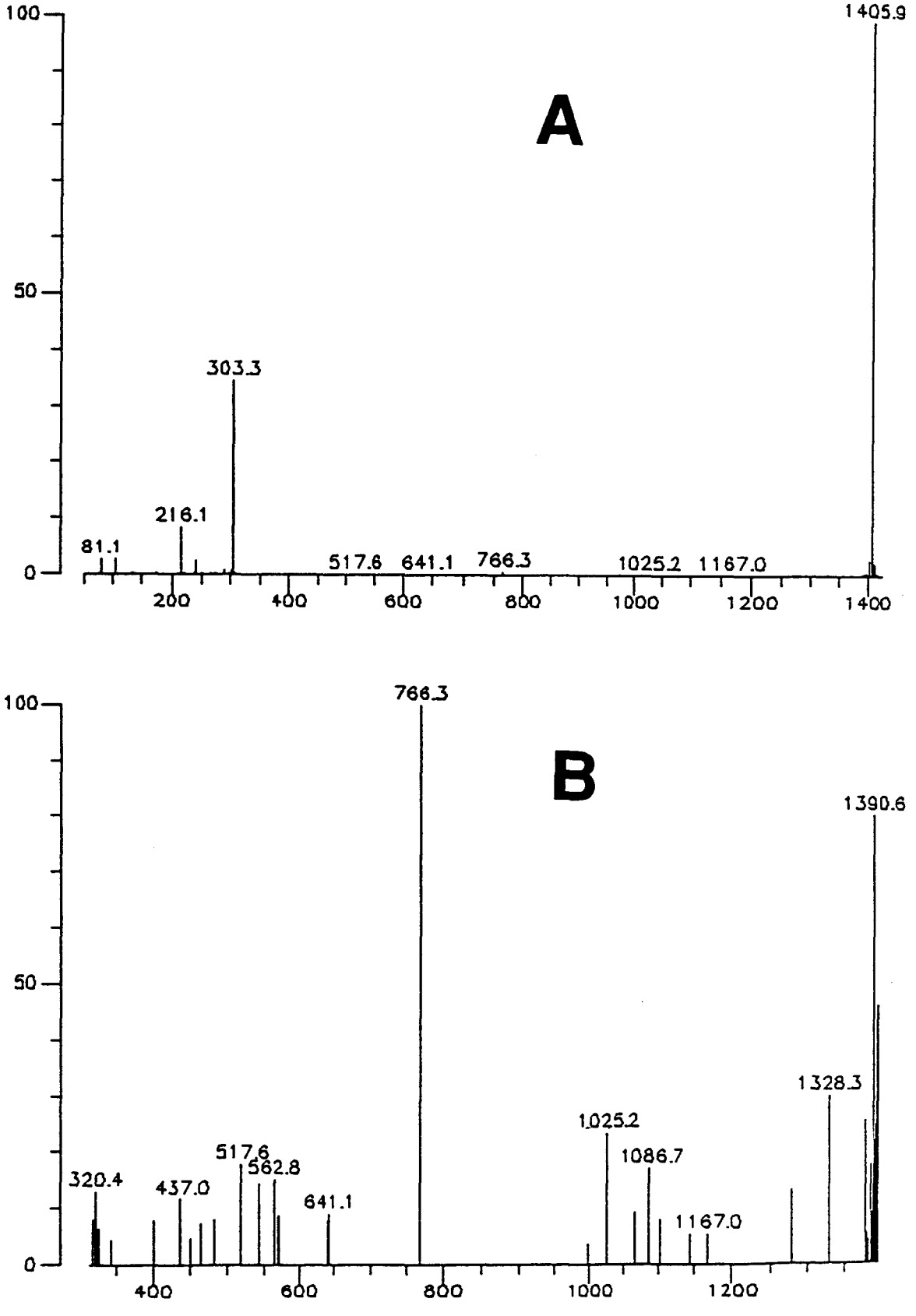


Figure 1. FAB MS/MS mass spectrum of fully protected dinucleotide D(GpC). The peak at mass 1406 was selected as parent ion. (A) Mass range 50-1425, (B) mass range 325-1400.

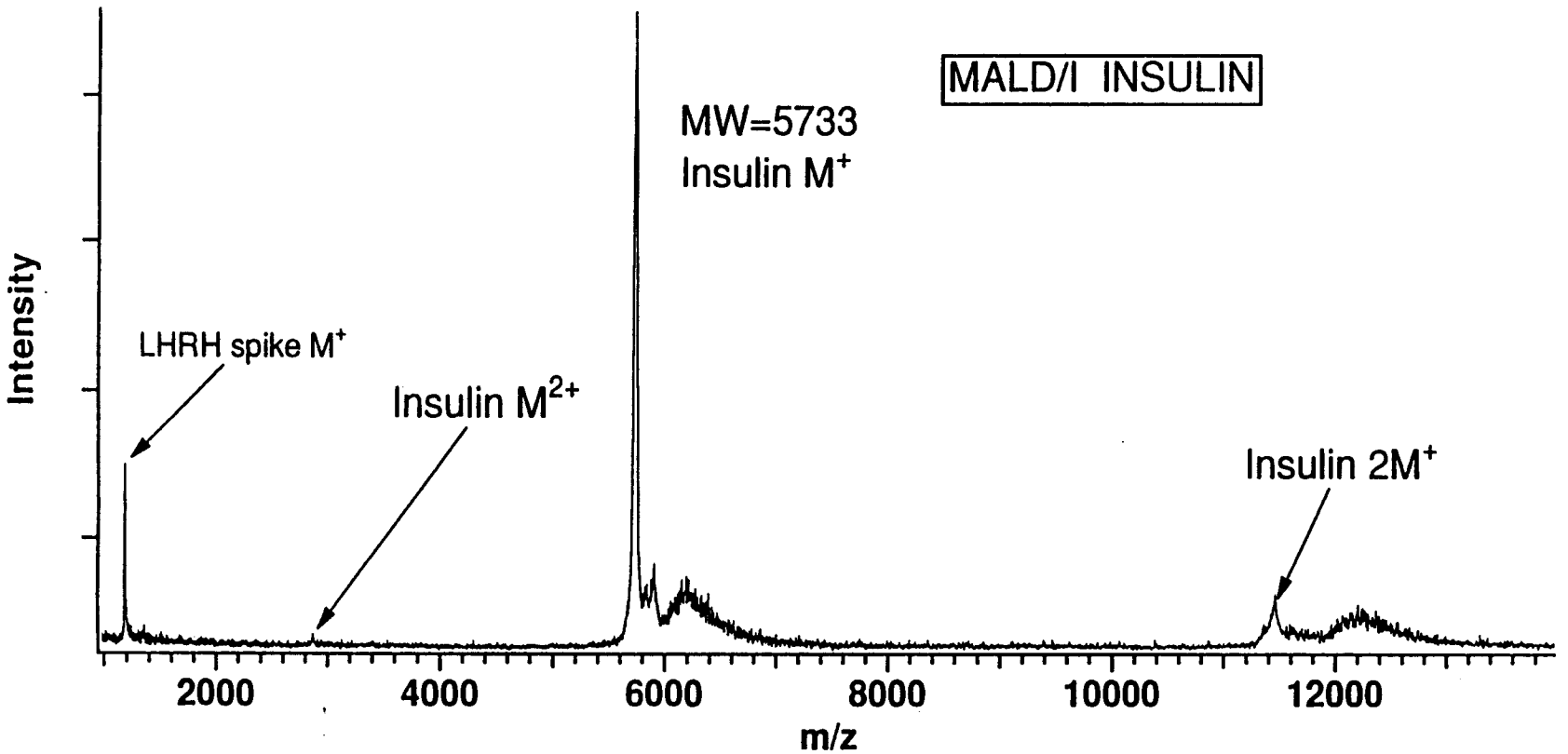


Figure 2. MALDI mass spectrum of insulin from our time-of-flight mass spectrometer. The laser conditions are: wavelength 337 nm at a power density of 2 x 10^6 Watts/cm^2. The resolution (FHWM) is 200 at m/z 5733.

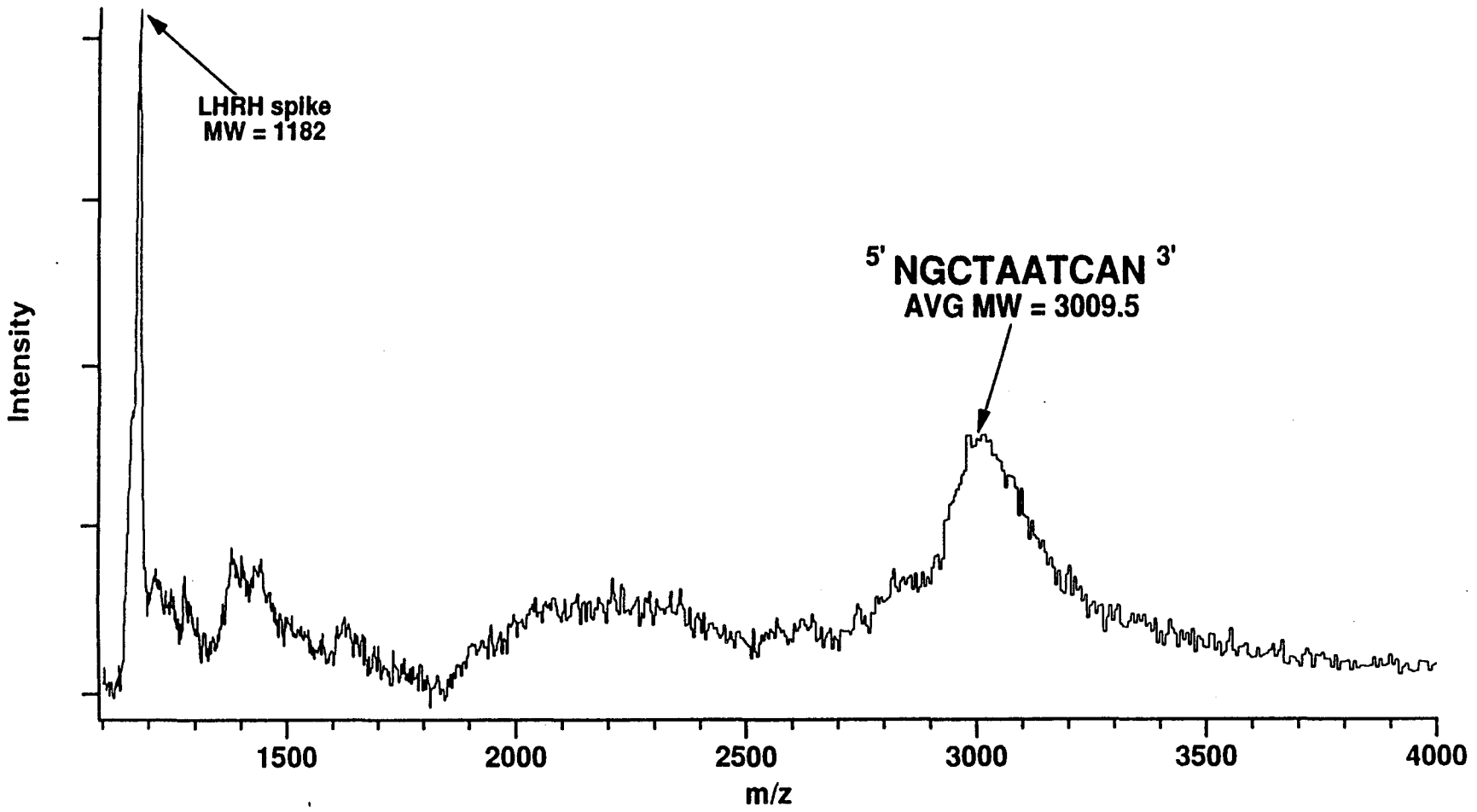


Figure 3. Negative ion MALDI mass spectrum of a series of oligodeoxynucleotide 10-mers. The notation N means that any of the four bases, adenine, cytosine, guanine or thymine are present. The LHRH spike is added for mass calibration.

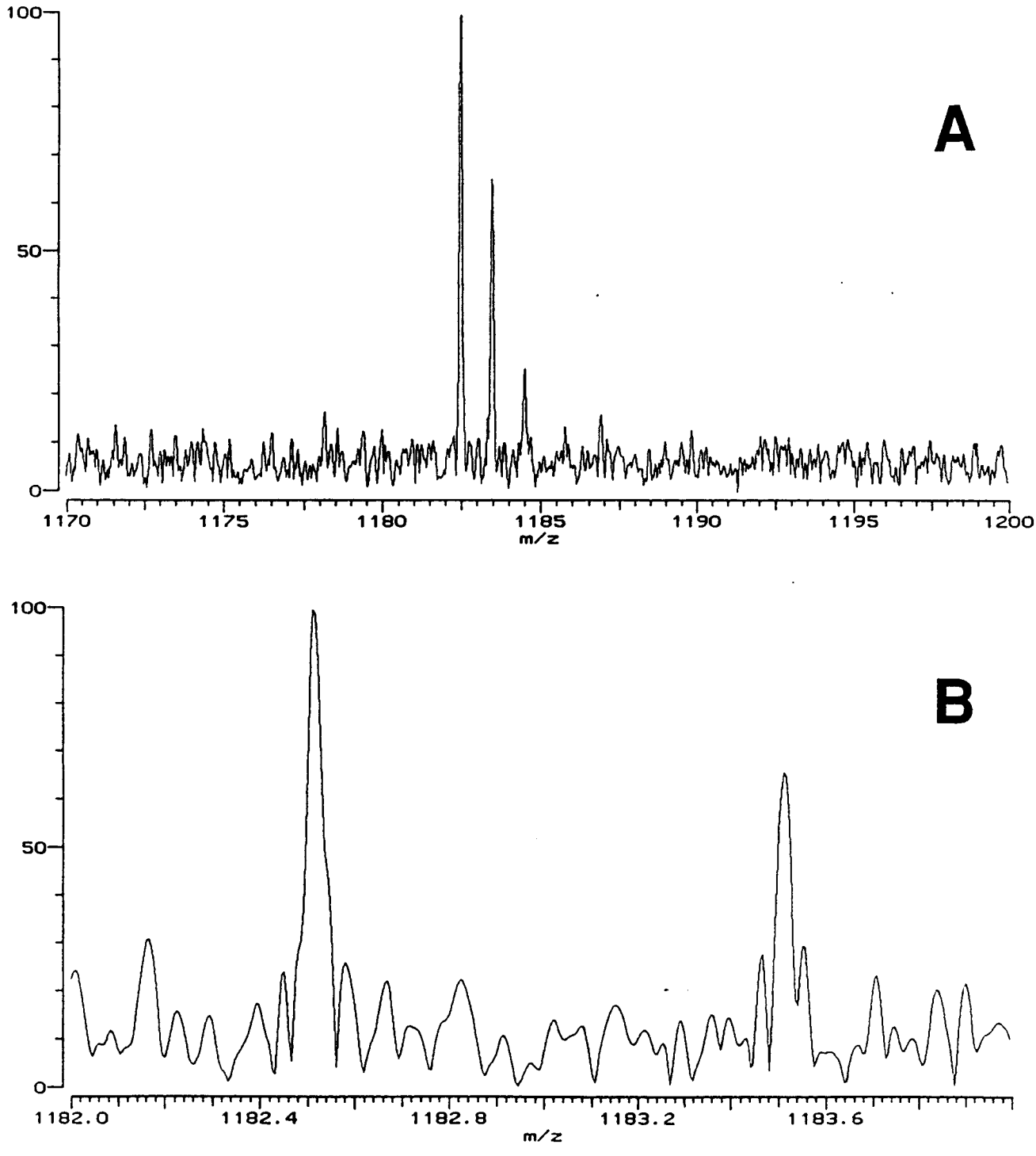


Figure 4. MALDI Fourier transform mass spectrum of LHRH (luteinizing hormone releasing hormone) molecular weight 1182. The ions observed are the protonated molecular ion and isotope ions. (A) resolution of 15,000 (B) resolution of 30, 000.

92-160 -- DESIGN ENZYMES FOR EFFICIENT AND EFFECTIVE CONVERSION OF BIOMASS INTO CHEMICAL FEEDSTOCKS AND FOR OTHER INDUSTRIAL APPLICATIONS

Associate Laboratory Director Area: Energy, Environmental, and Biological Research

Principal Investigators:
J.R. Frank, Energy Systems
M. Donnelly, Environmental Research
S.N. Kakar , Environmental Research
M. Schiffer, Biological and Medical Research
F.J. Stevens, Biological and Medical Research
S.P. Tsai, Energy Systems
R. Venkatadri, Energy Systems

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$329.5K
FY 1993	$305K
FY 1994	$315K

Purpose: The objective of this project is to develop new methods for the biochemical production of chemicals by designing modified enzymes that utilize substrates, produce products, or catalyze reactions that naturally derived enzymes are incapable of performing. This project will provide information that can lead to predictions of changes in enzyme specificity through specific modifications in the amino acid sequence of active sites, an approach that differs from the current trial and error method. This project draws together the multidisciplinary team needed to develop this new technology and best utilize the new parallel computing and Advanced Photon Source (APS) technologies that will become available in the near future. The disciplines that this project draws together include x-ray crystallography, biochemistry, molecular genetics, microbiology, and biochemical engineering. The project will develop capabilities at Argonne National Laboratory (ANL) that will enhance our ability to obtain programs in the strategically important area of bioprocessing.

Approach: The U.S. Department of Energy (DOE) and other government agencies have initiated several programs focused on producing chemicals from plant biomass and/or wastes as a substitute for petroleum-based chemicals or for the production of chemicals that have novel properties (e.g., biodegradability or stereospecificity). Previous approaches utilizing bioprocessing for chemical production have focused on low-volume, high-value chemicals through the use of, primarily, whole cell systems. Other processes produce bulk organic chemicals (such as glucose, ethanol, lactic acid, and butanediol) and utilize whole cell systems supplemented with enzymes. This project is creating a new technology in which bulk organic chemicals (such as glucose and lactic acid) can be converted to specialty chemicals currently produced from petrochemicals (e.g., acrylic acid). This new technology utilizes naturally occurring enzymes that have been modified to change their substrate specificity so that new substrates can be used to produce new products with fewer reaction steps that differ from those that occur in nature.

This study investigated a number of biochemical pathways and enzymes that were examined with regard to their ability to serve as model systems suitable for the development of this technology and for their potential to produce useful products. Criteria for selection included the availability of enzyme structure information, a suitable gene expression system, and products of potential commercial interest to DOE and other agencies. Mutants of the enzymes will be characterized with regard to changes in substrate specificity and other biochemical modifications. These data will then be used to develop a data base and models that can be used to predict modifications of enzyme specificity and characteristics on the basis of specific amino acid substitutions.

Several methods are being used to carry out this work. Selected model x-ray crystallography is being used to characterize the enzyme structures. Dr. J. Birktoft, Washington University School of Medicine, is collaborating with ANL researchers because of his previous work on one of the enzymes selected by the program for further study, malate dehydrogenase (MDH). In addition to determining structures of the enzymes, the project will make specific point mutations at sites affecting substrate specificity by utilizing genetic engineering techniques. These modified "mutant" enzymes will then be characterized biochemically. Work will also be carried out on methods to test modified enzymes in conditions that are more realistic. This task will include immobilizing these enzymes in reactors that use nonaqueous solvent systems so that the yield and rate of reaction can be maximized by restricting water activity.

Technical Progress and Results: During the first year of this project (FY92), a number of biochemical pathways and enzymes were analyzed to determine their potential for substrate modification and the production of useful products. It was determined that MDH was most suitable as a model system because it is highly characterized and has an excellent expression system. Moreover, some work on changing substrate specificity had already been carried out by an ANL collaborator at Washington University School of Medicine, so mutants were available for further analysis. Both thermophilic strains of *Thermus flavus* and hyperthermophilic strains of *Sulfolobus*, an aerobic archaebacter, are being utilized by ANL researchers in these studies. In addition, fumerate dehydratase or fumarase (FH) was selected because of the possibility that a product of high industrial interest (e.g., acrylic acid) could be produced by modifying substrate specificity. FH, however, has not been fully characterized and does not yet have a suitable expression system.

In FY93, MDH will be modified at specific sites, cloned, and produced by utilizing genetic engineering techniques. Modified MDHs will be produced and tested for changes in their specificity, activity, and stability. Microorganisms containing fumarase will be examined, fumarases will be characterized, and expression system development will be initiated. Bioprocessing conditions that favor the dehydration reaction catalyzed by fumarase and malate dehydrogenase will be identified.

Specific Accomplishments: The initial biochemical literature study and analyses have resulted in ANL obtaining the lead on biochemical pathways in DOE's Alternative Feedstocks Program. As a result of ANL's analyses, the DOE program has selected targets for work in FY93 of interest to ANL researchers, and ANL has retained an important role as the lead laboratory in biochemical and genetic pathway modification. While no DOE program funds will support the LDRD objectives in FY93 because of this project's longer-term goals, the DOE Alternative

Feedstocks Program has indicated interest in the approach and supported future funding by DOE's more basic research-oriented Advanced Industrial Concepts program. A recent review by DOE of this project at ANL, an exhibit at the Biobased Products Expo '92 held in St. Louis, and a presentation at DOE headquarters have all resulted in expressions of interest and the potential of future funding.

An invention disclosure has been submitted by S.P. Tsai and F. Stevens entitled "A Process for the Conversion of Lactic Acid into Acrylic Acid Catalyzed by a Modified Fumerase" (ANL-IN-92-060).

Discussions regarding potential collaboration are being conducted with Genencor International, which is the leading industrial biotechnology firm.

92-167 -- PROBING PHOTOSYNTHESIS WITH MOLECULAR BEAMS

Associate Laboratory Director Area: Physical Research

Principal Investigator: D. H. Levy, Chemistry
J. R. Norris, Chemistry

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$ 25K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: We investigated methodology to study electron transfer in photosynthetically relevant systems using molecular beam electronic spectroscopy.

Approach: Complicated molecular systems such as chlorophyll aggregates or model electron transfer complexes can be investigated with super high resolution spectroscopy when using supersonic jets to inject molecules into molecular beams. The ultra high resolution spectroscopy provides detailed information not otherwise available. This high resolution is a direct consequence of working in the gas phase at low temperature. An additional advantage of this approach is the lack of solvent molecules which complicate both the chemistry and the spectroscopy in liquids and solids.

Technical Progress and Results: The injection into molecular beams by supersonic jets of dimeric porphyrins as models of the special pair primary donor of photosynthesis certainly appears feasible. In addition, the connection between gas phase electron transfer experiments and electron transfer in photosynthetic reaction center proteins was compared. An important outcome is that the lack of solvent molecules in the gas phase produced novel results for electron transfer as studied by a molecular beam technique. Amazingly, the electron transfer in photosynthetic proteins has characteristics similar to electron transfer in the gas phase. In other words, the protein solvent acts as if it were not there, just like solvent molecules do not exist in the gas phase. This is in stark contrast to electron transfer in ordinary liquid or solid solutions.

Specific Accomplishments: The implication of this comparison between the gas phase electron transfer and the photosynthetic electron transfer process is significant for future artificial photosynthesis programs. Our results suggest that restricted solvent configurations, such as that which exists in proteins, can be designed in such a manner as to present very little barrier to electron transfer and thereby increase the energy stored in the products of a photochemical reaction.

Publications Include:

"Intramolecular Electron Transfer in a Molecular Beam", Chattoraj, M., Laursen, S. L., Paulson, B., Chung, D. D., Closs, G. L., and Levy, D. L., Journal of Physical Chemistry, in press.

92-169 -- DNA SEQUENCING BY HYBRIDIZATION: SOFTWARE DEVELOPMENT FOR GENOME SEQUENCING RECONSTRUCTION

Associate Laboratory Director Area: Energy, Environmental and Biological Research

Principal Investigators: R. Crkvenjakov, Biological and Medical Research

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$ 36.1K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: DNA sequencing methods have to improve over several orders of magnitude to answer to the needs of DOE sponsored Human Genome Project. The Sequencing by Hybridization (SBH) approach has a demonstrated potential for achieving this. Beside biochemical/molecular biological and instrumentation components currently under intensive development, a computational component is particularly important. BIM's SBH group has immediate needs in production of software needed for achieving convincing simulations of sequence reconstruction. This requirement has a narrow time frame, since demonstration of the utility of the approach must include these computational aspects.

Approach: The effort focused on developing appropriate computational science algorithms as well as a library of utilities which are applicable in immediate and future applications. We investigated, developed and implemented computational techniques as well as evaluated and utilized appropriate computer architectures. With regard to software implementation, we developed software for:

1. A workstation environment

2. A vector supercomputer, e. g., the CRAY XMP/18 in CTD.

In addition, we evaluated the scalability of our work and the computational requirements of sequencing a million base pairs for massively parallel systems such as the Intel Touchstone Delta.

The software utilities were applied in prototype applications to demonstrate their capability. These implementations were developed in a compatible manner so that the same application can be run on both systems, as appropriate.

Technical Progress and Results: In collaboration with staff members in the Computing and Telecommunication Division we have investigated the potential of various parallel architectures for human genome sequencing by the hybridization method. Our efforts have focused on the development of algorithms for creating logical tables and extension sequences necessary for use in heuristic optimization approaches to solving the hybridization problem. We developed several algorithms and the necessary analysis for their storage requirements. These algorithms were implemented in a portable manner for distributed computation (using the P4 package developed

at ANL). Preliminary results demonstrate that we can develop the necessary logical tables and expansion sequences for problems involving 350,000 base pairs on the Intel Touchstone Delta in from 30 seconds to several minutes (depending upon the length of the expansion sequence). Results were also obtained for a distributed network of workstations, individual high-performance workstations and a Cray XMP/18. These results are documented in a report by L. Revor (Fall 1991 SERS (Science & Engineering Research Student) participant). Future work should focus on exploiting these results in reconstruction algorithms and treating larger (and more realistic) problems on massively parallel systems.

Specific Accomplishments:

1. Developed a software library of computational kernel routines for use in sequencing for both a workstation and Cray supercomputer.

2. Conducted benchmark computations to illustrate the utility and scale of the developed software.

3. Examined and reported on the scalability and requirements of the resulting software to massively parallel computer systems.

Internal Report

"Algorithm Design and Optimization for Genome Sequencing," Revor, Louis S., submitted to Computing and Telecommuncations Division (CTD) and Division of Educational Programs (DEP), January, 1992.

92-173 -- At-211 LABELED ANDROGENS FOR CANCER THERAPY

Associate Laboratory Director Area: Energy, Environmental and Biological Research

Principal Investigator: R.W. Atcher, Chemistry
B. Shafii, Chemistry

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$ 40.5K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: To design compounds that can be labeled with At-211 to target the androgen receptor in cancer tissue. This objective can only be met by developing the chemistry necessary to perform this labeling quickly and in high yields.

Approach: We set out to improve the current labeling chemistry for radiohalogenation of small molecules. This can be accomplished in two ways. First, improve the synthesis of the receptor binding compounds to reduce side products that are difficult to separate and to improve the stability of the precursor compounds.

In collaboration with Dr. Eugene DeSombre at the Univ. of Chicago, we have been working on the use of steroidal hormone receptor binding compounds for the diagnosis and therapy of appropriate tumors. Our work to date has focused on the estrogen receptor binding compounds. These are present in tumors of the female reproductive system. We wanted to expand our studies to the androgen receptor for two reasons. First, the androgen receptor is associated with tumors of the male reproductive system, specifically the prostate. Second, there is mounting evidence that the androgen receptor plays a complementary role to the estrogen receptor in gynecologic tumors.

We began fundamental studies of the chemistry of halogenation by focusing on two aspects. First, we wanted to improve the specific activity of the radiolabeled material by decreasing the amount of halogenation by bromine and chlorine. Second, we wanted to explore "leaving" groups that were less bulky than tributyl tin derivatives which have been used to date. An added bonus to other organometallic derivatives would be the improved shelf life of the precursor compound.

Technical Progress and Results: To date, we accomplished three significant aims in this work. First, we determined that we could achieve high halogenation yields by using a nitric acid oxidation scheme that would only oxidize iodine and astatine. This would eliminate the bromination and chlorination reactions that one finds if a hydrogen peroxide/acetic acid system

is used. In a variety of experiments, we optimized this chemistry using I-125 as the model radionuclide for labeling.

The second aim of this project was to explore the use of organometallic precursors other than tributyl tin derivatives. The tributyl tin group has two characteristics which present problems in labeling. First, the tributyl tin group is not stably attached to the precursor compound. It has to be kept at -80° C or colder to maintain the chemical integrity of the compound. In halogenation reactions, it is large enough to inhibit the approach of the halogen to the target carbon atom. To achieve our aim, we developed the synthesis of trimethyl silicon and trimethyl germanium compounds. These have the advantage of less steric hindrance and a long shelf life even if kept at room temperature. Thus, labeling yields should increase and the precursors are more stable when stored.

Specific Accomplishments: The halogenation in nitric acid has been submitted as a manuscript to Applied Radiation and Isotopes. An invention report was also submitted on this work. The manuscript for the preparation of the trimethyl silicon and trimethyl germanium compounds is in preparation.

An FWP for FY 1994 has been submitted to OHER for funding the continuation of this work.

92-180 -- HYPERTHERMOPHILIC BACTERIAL BIOCHEMISTRY AND MOLECULAR BIOLOGY

Associate Laboratory Director Area: Energy, Environmental and Biological Research

Principal Investigator: M. J. Peak, Biological and Medical Research

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$ 47.5K
FY 1993	$195K
FY 1994	$267K

Purpose: The purpose of this research is to develop a new capability in the Biological and Medical Research Division at Argonne National Laboratory (ANL) for research into the basic biology, enzymology, and molecular biology of a recently discovered group of novel microorganisms that flourish near and even above the boiling point of water, the hyperthermophilic Archaea. They are the most ancient life forms known at present and they are at the very frontiers of biological research, only growing in extremely hot environments such as marine volcanic vents. Basic research in this program will include enzymology, gene cloning and sequencing, and investigations into DNA repair. Future applications and benefits will be the opening of new horizons in protein structure and function using x-ray crystallography, ultimately as a new program at the ANL Advanced Photon Source; high-temperature catalysis and its industrial applications, especially as a tool in the DOE Biomass Conversion into Chemical Feedstocks Program; and molecular biotechnology applications of site-directed mutagenesis for optimizing enzyme catalysis in industrial application.

Approach: It is proposed that the new program be multifaceted, and several existing programs already in existence at ANL will be able to contribute to the new initiative and will themselves be enhanced by the interaction. For instance, protein structure will be analyzed by x-ray crystallography in the group of M. Schiffer (BIM); site-directed mutagenesis (D. Hansen, BIM) will create new and useful enzyme catalysts for biotechnological purposes; cloning of the enzymes into mesophilic organisms such as *Escherichia coli* will allow preparation of massive amounts of pure protein, with DNA sequencing providing insights into the molecular genetics of these organisms as well as help elucidate mechanisms whereby they function in boiling water.

M. J. Peak has been collaborating with M. W. W. Adams' laboratory (Biochemistry Department, University of Georgia) to investigate the fundamental biochemistry (enzymology) of the hyperthermophilic archaea.

Technical Progress and Results: During this period cultures were grown of one eubacterium and four archaean microorganisms, all hyperthermophilic. In order to elucidate the basic biochemistry of these organisms, a survey of some 26 enzyme activities from the major metabolic pathways has been performed in cell-free extracts of the organisms. Another purpose of this study was to pinpoint specific enzymes for future investigation. Table 1 demonstrates the results of the preliminary survey.

Clearly these organisms do not have "classic" metabolism. The lack of complete Krebs cycle activities is consistent with the facultative anaerobic lifestyle of these organisms. Presumably the enzymes that were found act in either anabolic or catabolic sequences of other pathways, yet to be elucidated. Enzymes involved in the glycolysis and gluconeogenesis pathways are more completely represented in most of the organisms, and the lack of phosphoenol pyruvate carboxylase confirms the absence of the Krebs cycle, since the function of this activity lies in anaplerotic refeeding of the cycle.

The activities enolase, aldolase, and also glycerate kinase (not shown in Table 1) were selected for purification and further study. At the time of writing, enolase from *P. furiosus* is in the process of being completely purified.

Specific Accomplishments:

Insights into the laboratory culture and lysis of a range of hyperthermophilic microorganism have been gained, as well as into their intermediary metabolism. Techniques in enzyme purification under stringently anaerobic conditions have been perfected; some of the enzymes from these organisms are exquisitely sensitive to ground-state oxygen, requiring that all manipulations during purification be performed anaerobically. A manuscript is in preparation (M. J. Peak and M. W. W. Adams, Comparison of 25 enzyme activities from a hyperthermophilic eubacterium and four hyperthermophilic archaea: glycolysis, Krebs cycle, gluconeogenesis and related activities. J. Bacteriol.).

Table 1. Enzyme activities from hyperthermophilic microorganisms[a]

Pathway/Enzyme	*Thermotoga maritima*	*Pyrococcus furiosus*	*Thermococcus litoralis*	ES1	ES4
KREBS CYCLE					
Cit.synthase[b]	524	0[c]	0	0	0
Aconitase	0	0	0	0	0
Fumerase	133	0	0	80	0
MDH/NAD	0	0	0	0	0
MDH/NADP	0	0	0	0	0
ICD/NAD	0	0	0	0	0
ICD/NADP	849	0	0	33	0
αKDH/NAD	0	0	0	40	0
αKDH/NADP	0	0	0	102	0
GLYCOLYSIS					
Aldolase	2030	615	217	0	14
GaPDH/NAD	0	0	0	0	0
GaPDH/NADP	16	180	77	100	160
Enolase	1590	2430	718	620	400
Pyr.kinase	1800	770	2170	2300	18200
LDH/NAD	0[d]	0	0	0	0
LDH/NADP	0	0	0	0	0
ADH/NAD	0	31	0	77	0
ADH/NADP	0	46	109	3170	0
GLUCONEO-GENESIS					
6PGD/NAD	14	12	0	0	21
6PGD/NADP	23	100	320	66	54
G6PD/NAD	0	0	0	0	36
G6PD/NADP	14	41	82	19	36
OTHER					
PEPC	0	0	0	0	0
GtDH/NAD	0	46	0	0	0
GtDH/NADP	0	12150	0	0	3790

[a]OD Units per min per g protein
[b]Abbreviations: cit., citrate; MDH, malate dehydrogenase; NAD, nicotinamide adenine dinucleotide; NADP, NADP, nicotinamide adenine dinucleotide phosphate; ICD, isocitrate dehydrogenase; α-KDH, α-ketoglutarate dehydrogenase; GaPDH, glyceraldehyde-3-phosphate dehydrogenase; Pyr., pyruvate; LDH, lactate dehydrogenase; ADH, alcohol dehydrogenase; 6PGD, 6-phosphogluconate dehydrogenase; G6PD, glucose-6-phosphate dehydrogenase; PEPC, phosphoenol carboxylase; GtDH, glutamate dehydrogenase.
[c]No activity detected
[d]But see Wrba *et al.*, Eur. J. Biochem. 188, 195-201 (1990)

92-043 -- A PILOT PROGRAM FOR THE STUDY OF THE RELATIONSHIP BETWEEN LEUKEMIA AND LOW-LEVEL RADIATION IN BYELORUSSIA

Associate Laboratory Director Area: Engineering Research

Principal Investigator: Y. Orechwa, Reactor Analysis

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$123.3K
FY 1993	$100K
FY 1994	$100K

Purpose: The project initiated a pilot study to test, prior to any international agreement and significant investment of funds, the feasibility of a cooperative program for studying the relationship between the incidence of leukemia in a human population and low non-trivial chronic radiation doses in the Gomel administrative district of the Republic of Byelarus. A large fraction of the territory of the Republic of Byelarus, in particular the administrative district of Gomel, has been affected by non-trivial quantities of radioactive contamination due to the nuclear power reactor accident of Chernobyl. That this contamination has had serious health consequences has been demonstrated by the dramatic increase in the incidence of thyroid cancer in children in the Gomel district of Byelarus (Nature, Vol. 359, 3 September 1992). The question of a concomitant increase in the incidence of leukemias is both central and timely. The project is based on the novel approach of replacing a large-scale controlled epidemiological study with small-scale focused studies which use state-of-the-art molecular biology. The objective is to create at ANL a long-term program which brings together the largest source of in-vivo data on the effects of low-level radiation on a human population, the ANL capabilities in radiobiology, and the world's leading center in the cytogenetic studies of secondary leukemias at the University of Chicago.

Approach: It is universally accepted that the risk of leukemia must be formulated from leukemia experience of irradiated humans, since the relative sensitivity for the induction of different effects (leukemia, bone sarcoma, tumors of soft-tissue near bone, etc.) is probably different in different species. Therefore, simple ratios of various effects at various exposure levels in experimental animals cannot be applied directly to man for leukemia induction since there is a dearth of information about the induction of leukemia in man by internal irradiation. This cooperative program offers the unique opportunity to address this issue. There are three basic objectives to the program: overall feasibility, database development and analysis of biological samples. The division of labor in this cooperative study is to be along the lines of comparative advantage -- molecular biology being the main responsibility of ANL, while dose reconstruction and tracking of individuals for study being the main responsibility of Byelarus.

Given the socio-economic upheaval in the republics of the former USSR, it is critical that the feasibility of all aspects of the cooperative project be established. The effort in FY 92 has primarily addressed this issue. An institutional tie has been developed between ANL and the International Sakhanov College of Radioecology (ISCR) in Minsk, Byelarus. Some working relationships have been established and are in effect. Critical to the effort is the transfer of

biological material from Byelarus to ANL. That is, issues such as whether the material is obtainable, will it be released, and can it be transported in a form amenable for analysis and archival storage.

The database contains two types of information - dosimetric and biological. Because the project is dealing with a dynamic situation, the creation of this database is a continuous process. In radiobiology dosimetry is critical. (It should be kept in mind that nearly 50 years after the bombings at Hiroshima and Nagasaki, the dosimetric estimates are still being adjusted to the extent that they affect the dose-effect relationships.) A novel approach is applied in which three techniques are applied simultaneously when possible. Two are biological dosimetry methods - chromosomal analysis in lymphocytes, and electron spin resonance analysis of tooth enamel or bone specimens. The third method is the application of the traditional physical dose reconstruction techniques.

Critical to this project is the acquisition of human material from humans at high risk of development of malignancies. The biological database consists of cytogenetic information from samples of human periferal blood and/or bone marrow of leukemia victims from the Gomel administrative district in Byelarus. In addition, a portion of the sample of viable cells is stored for archival purposes. It is expected that given the rapid development in analytic techniques in the field of molecular biology, this archival collection of unique and irreplaceable data is likely to be instrumental in advancing human radiation biology as the field further progresses.

Technical Progress and Results: In order to maintain a database and perform the physical dose reconstruction a personal computer with appropriate software and periferal equipment was sent to the ISCR in Minsk.

For the measurement of the radioisotopes of Sr (a bone seeking element and therefore important with regard to passible leukemia induction) a surplus lowbeta II gas spectrometer was obtained from the DOE Environmental Measurement Laboratory in New York and shipped to Minsk.

An extensive questionnaire composed of, passport, medical, family, residence and socio-economic information, and the history of radiation exposure was formulated. This information has been gathered for children who were under the age of 14 at the time of the Chernobyl accident and subsequently contracted leukemia.

A blood sample from four victims was obtained and hand carried to ANL. Each sample was divided into three parts, one for archival storage at ANL, one for cytogenetic analysis in Prof. Janet Rawley's laboratory at the University of Chicago, the other for biological dosimetry at Lawrence Livermore National Laboratory.

Measurements and statistical analysis have been performed of the Cs-137 transfer coefficient from soil to milk in the Gomel district. In all cases the data indicated a nonlinear (inversely proportional) dependence of the transfer coefficient of Cs-137 from soil to milk in the activity interval 1 - 10 Ci/km^2. This implies that the concentration of Cs-137 in milk in the interval 1 - 10 Ci/km^2 does not depend on the concentration of radionuclides in the soil. This result is likely to simplify some of the mathematical modeling and reduce uncertainties.

The FY 92 results indicate, that in addition to the continuation of the development of the database, in FY 93 a substantial emphasis will be placed on the preparation in Byelarus of biological samples and some of the analyses according to protocols used at the University of Chicago.

This will greatly improve cell survival and make analysis more efficient.

Specific Accomplishments: Submitted for translation and publication, "Correlation Analyses: Interrelation of the Concentration of Cs-137 in Feed Grass and Soil," O. V. Konchin and I. V. Rolevich.

Report due December 1, 1992 on the physical dose reconstruction for the four victims whose blood was analyzed.

91-010R1 -- MODELING AND REMOTE SENSING OF GLOBAL TERRESTRIAL ECOSYSTEMS

Associate Laboratory Director Area: Energy, Environmental, and Biological Research

Principal Investigator:
M. L. Wesely, Environment Research
A. P. Campbell, Environmental Assessment and Information Sciences

Funding Profile:

FY 1990	$ 0K
FY 1991	$313K
FY 1992	$265.1K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: This work is designed to develop innovative methods for the modeling and remote sensing of global terrestrial ecosystems, to evaluate the effects of potential climate change on biota and the consequential feedbacks to the Earth's climate system. In Environmental Research (ER), research concentrates on simulating physiological and biophysical processes of vegetation to allow the quantitative description of biosphere-atmosphere interactions and on incorporating the simulations into atmospheric general circulation models (GCMs). In Environmental Assessment and Information Sciences (EID), research focuses on methods to analyze hyperspectral data of the type to be produced by future satellite systems, to produce advanced quantitative evaluations of surface properties and to detect changes in terrestrial ecosystems. Techniques established to detect and measure the effects of climate change may ultimately be used in conjunction with the effort to model global terrestrial ecosystems, to provide data for planning and gauging international responses to changes that might occur. This work has been incorporated into ANL's Global Climate Change Program under the direction of Dr. Ruth Reck of ER.

Approach: A major challenge in anticipating the environmental consequences of increased levels of CO_2 and other greenhouse gases is to model global climate change and quantify its effects on biota. To meet this challenge, global models of atmospheric, hydrologic, oceanic, and terrestrial and aquatic ecological processes need to be improved and coupled so that linkages and feedbacks can be realistically simulated. Modeling efforts for this project focus on the weakest component: terrestrial ecosystem models. Efforts to date to combine and extend ecosystem models over global scales have been very limited, partially because the models are developed by ecologists with different research specialties and are often controversial. Nevertheless, global terrestrial ecosystem models are necessary to describe – in terms of surface energy balance, hydrological balance, and the carbon cycle interactions between the atmosphere and biota over periods of decades and longer. With the improvements in climate models and computer capabilities that will occur in the 1990s as a result of efforts such as DOE's Atmospheric Radiation Measurement (ARM) and Computer Hardware, Advanced Mathematics, and Model Physics (CHAMMP) programs, the opportunity exists to begin complementary work on global terrestrial ecosystem models.

To model global terrestrial ecosystems, extensive ecological information is being gathered and incorporated into a framework that can be used by an existing GCM or other large-scale numerical models. The process of scaling up from small to large spatial areas involves several steps and is quite complicated. Land cover types, each with separate responses to environmental conditions and with various types and rates of atmosphere-biosphere exchanges of mass and energy, must be aggregated into forms that can be used to describe both exchange and ecological processes in biogeochemical models for specific biomes. An existing biophysical model provides the connecting point between biogeochemical models and large-scale climate models, which require extensive parameterization of variables involving atmosphere-biosphere exchange. The overall numerical modeling effort must provide for efficient transfer, among all levels of simulation, of data on environmental and air-surface exchange.

Our approach includes an extensive effort to develop the overall modeling framework, but the work's most crucial aspect is the ecological modeling itself. That is, satisfactory descriptions must be developed for ecological responses in terms of the surface accumulation of carbon, the exchange of greenhouse gases, evapotranspiration, and the basic functioning that affects the viability of competing plant species. Furthermore, the descriptions must be efficiently parameterized so that long-term simulations can be accomplished.

Constructing an inventory of surface properties that affect climate change requires extensive information on the physiological and nutrient status of vegetation. Large-scale inventories are particularly difficult. Past work has shown that optical remote sensing data obtained with satellites can be used to detect vegetative conditions. However, these data are limited to the rather sparse information in the four or five optical wavebands that are now most commonly used. As a result, a portion of this work focuses on developing techniques for using more advanced remote sensing data to monitor changes in global terrestrial ecosystems. Hyperspectral imagery, which currently consists of 210 narrow spectral bands (10 nm) between the long ultraviolet (400 nm) and middle infrared (2500 nm), is used in this study. Acquisition of hyperspectral imagery from satellites might occur within the next ten years. For example, the Jet Propulsion Laboratory (JPL) developed and flew on aircraft a set of instruments that collect hyperspectral image data. In addition, JPL and the U.S. Engineering Terrain Laboratory (ETL) have used mostly laboratory determinations to compile a database of over 1000 surface spectra, including reflected and emitted energy spectra for a wide variety of natural and man-made surfaces. To be useful, this information must be related to features that occur naturally at the surface of the earth. Because image pixels observed from aircraft and satellite platforms often include returns from surfaces with various proportions of coverage by different types and conditions of vegetation, the spectral responses for a pixel usually do not accurately match the spectra in the database. Our approach to this problem has been first to develop tools to allow automatic handling of the huge amounts of data collected and then to use the tools to manipulate the data in various ways and examine relationships between measured surface spectra and those compiled in the database.

Data from high-resolution imaging spectrometers are a powerful new means to gain a better understanding of the Earth's surface layers. Such instruments generate hyperspectral "image cubes" containing spatial images for up to several hundred different wavelength bands, allowing spectroscopic analysis techniques to be applied to every pixel in an image.

A prototype hyperspectral imagery analysis software system being developed and tested employs artificial intelligence techniques and other advanced approaches to deduce surface characteristics and extract features from the hyperspectral images. Among its capabilities, the prototype system can classify image pixels by neural network analysis of data including the pixel radiance or reflectance spectra and other image metrics (e.g., image "texture spectra" derived from the fractal dimensions and fractal signatures computed for subimage tiles at each wavelength).

Technical Progress and Results: A key determinant of terrestrial ecosystem responses to climate change is the climatic tolerance of plants. Current approaches make an assumption that the climatic tolerance of trees can be assessed by an examination of geographic range. On this basis, extreme sensitivity of Boreal forests to climate change has been predicted. This approach, however, might produce a biased result because tree geographic ranges result not only from climate tolerance but also from competitive interactions. Data were collected on Boreal trees growing in southern botanical gardens to assess true climatic tolerance. These data suggested far greater climatic tolerance than prior studies had assumed (e.g., white spruce could grow in the Appalachian foothills in North Carolina).

Global carbon cycle models have been used in attempts to account for sources and sinks of carbon. These models suffer from uncertainties and problems such as unknown equilibration times for ocean-atmosphere interactions. Because a longer time scale might elucidate these factors, data from ice cores and other sources over the last 160,000 years were analyzed. Various investigators had suggested that geologic methane emissions could be an overlooked source term for atmospheric CO_2, but the source term seemed too small to consider under current human input regimes. Over longer time periods such as the glacial cycles, however, geologic sources might be more significant. A simple carbon cycle model, the hydrocarbon pump model, was developed and parameterized to test the role of methane as a source for CO_2. This model predicted the magnitude, timing, and loss terms for atmospheric CO_2 changes over the ice age cycles. Carbon-14 and carbon-13 data supported methane as a source for CO_2 changes over the glacial cycles. The manuscript reporting this work is under internal review. An invitation has been received to visit NASA in Washington to present this work.

A crucial parameter in models of climate change due to CO_2 is the radiative forcing that results from increased CO_2. Other factors may produce compensating forces such as clouds or atmospheric circulation patterns. One approach for estimating the strength of this effect is to evaluate the statistical improvement in fit that results from adding a CO_2 term to the radiative forcing resulting from the variations in the Earth's orbit (the Milankovitch cycle). Our study challenges those results by showing that several historical factors are highly correlated statistically with CO_2 over the last 160,000 years and thus confound interpretation of the radiative forcing effect. These factors include methane levels, ice-free land area, and ocean circulation – all of which (like CO_2) amplify warming – and sulfate level, which has a cooling effect and is inversely correlated with CO_2. When these confounding factors are removed, the remaining radiative forcing due to CO_2 may not be very strong. The manuscript describing this work is under internal review. An invitation has been received to visit NASA in Washington to present this work.

In Fiscal Year 1991, the remote sensing field for multispectral and hyperspectral data sources was surveyed, and advanced imagery exploitation techniques were investigated. On the basis of this survey, we obtained actual hyperspectral image data collected by the JPL's Airborne Visible/Infrared Imaging Spectrometer (AVIRIS). We selected artificial neural networks as a technology likely to be effective in analysis of hyperspectral images.

In Fiscal Year 1992, a software system for effective exploitation of hyperspectral image data was designed, implemented, and tested. The prototype software system is object based and is written in the C++ language. The system employs an easily assimilated graphical user interface for data navigation and visualization and a flexible data interchange scheme to allow the system to function independently of the source of hyperspectral data. To explore the options for optimal access to external image and related data, we developed two software system prototype variants, one interfacing with external image files in the University Corporation for Atmospheric Research's netCDF standard format, and one tightly integrated with a true object database.

The first major capability implemented in the prototype image analysis workbench was classification, with a neural network classifier, of image pixels into abstract surface types on the basis of image data from JPL's AVIRIS sensor system. Image pixels were classified by using a back-propagation neural network simulator.

The next major capability to be built into the system was computation of local fractal signatures for subtiles of an image. Fractal signatures can be thought of as curves of fractal dimensions of the image surface (represented as gray-scale values) as a function of the image distance scale. These measures of local image texture at various wavelength channels provide a valuable additional context for the determination of surface type for image pixels.

System testing has been based on AVIRIS images for the Jasper Ridge Biological Preserve and Moffett Field, both located near Stanford University in Palo Alto, California. On the basis of aerial photographs, topographic maps, and limited site reconnaissance of the Jasper Ridge area, we selected a coarse set of abstract surface types: water, meadow, lawn, paved, forest, etc. We then selected a few (typically seven to ten) examples of each type from the image and trained the net to classify all pixels in an image into one of these types.

To classify pixels by surface type, we have used both three-layer and four-layer back-propagation neural networks. Initially, the network has been configured with an input layer that simply has one input node for each wavelength channel, an output layer with an output node for each defined surface class, and one or two hidden layers. Using this configuration, we have had good success in producing high-resolution land use mappings without spending much time and effort in relating the site to ground truth or developing complex metrics based on domain knowledge to differentiate surface types. A neural network classifier trained on the Jasper Ridge data also had good success in classifying pixels in the Moffett Field image, indicating that this relatively simple approach is at least somewhat robust.

Specific Accomplishments:

Publications:

Loehle, C. "CO_2 and Historical Climate Change: Correlation versus Causation." Draft manuscript in internal review.

Loehle, C. "Geologic Methane and a Source for Post-Glacial CO_2 Increases: The Hydrocarbon Pump Hypothesis." Draft manuscript in internal review.

Miller, N.L., and I.T. Foster. "A Proposed Heirarchical Framework for Coupling Biogeochemical Trace Gases to a General Circulation Model." Submitted to *Journal of Climate*.

Presentations:

Miller, N.L. "Hierarchical Framework for Coupling a Biogeochemical Trace Gas Model to a General Circulation Model." North Atlantic Treaty Organization, Advanced Research Workshop on the Atmospheric Methane Cycle: Sources, Sinks, Distributions and Role in Global Climate Change, 7 October 1991, Mt. Hood, Oregon.

Miller, N.L. "Global Climate Change." Environmental Law Class, University of Denver, 9 April 1992, Denver, Colorado.

Miller, N.L. "A Framework for Coupling Biogeochemical Surface Fluxes to General Circulation Models." Meeting of the Midwest Association for Cloud and Aerosol Physics, 22 May 1993, Argonne National Laboratory.

We have described our work in hyperspectral imagery analysis at the Hyperspectral Digital Imagery Collection Experiment (HYDICE) meeting, held September 23-24 in Las Vegas, Nevada. The HYDICE committee will evaluate our prototype as the potential basis for the common analysis system of choice for its members (which include U.S. Department of Energy, U.S. Department of Defense, U.S. Department of Transportation, U.S. Department of Commerce, Central Intelligence Agency, National Aeronautics and Space Administration, National Oceanic and Atmospheric Administration [NOAA], and U.S. Department of Agriculture), under the direction of the Naval Research Laboratory.

Numerous other agencies have expressed a strong interest in our prototype hyperspectral software, particularly as an aid to coastal, offshore, and wetland ecological studies. Among these are the Florida Keys National Marine Sanctuary, the Florida Department of Natural Resources, the Florida Marine Research Institute, the NOAA Nautical Charting Research Division and Charting and Geodetic Services Branch, and the U.S. Environmental Protection Agency Region IV project office for Advanced Identification of Wetlands.

Hyperspectral presentations have been accepted at the following conferences:

- Sixth Artificial Intelligence Research in the Environmental Sciences (AIRIES) Workshop, Monterey, California, 27-29 October 1992.

- International Symposium on Spectral Sensing Research (ISSSR), Maui, Hawaii, 15-20 November 1992.

- Ninth International Conference on Interactive Information and Processing Systems (IIPS), Anaheim, California, 17-22 January 1993.

92-172 -- MODELING OF GLOBAL TERRESTRIAL ECOSYSTEMS*

Associate Laboratory Director Area: Energy, Environmental, and Biological Research

Principal Investigators: C. S. Loehle, Environmental Research Division
M. L. Wesely, Environmental Research Division

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$ 49.1K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: This work is designed to develop the innovative modeling and analysis approaches required to evaluate the effects of potential climate change on biota and the consequential feedbacks to the Earth's climate system. The research concentrates on developing mathematical methods to describe biotic and physical features of the Earth's surface. Efforts to model global terrestrial ecosystems will yield new information for planning and gauging international responses to potential changes. This work has been incorporated into ANL's Global Climate Change Program under the direction of Dr. Ruth Reck.

Approach: A major challenge in anticipating the environmental consequences of increased levels of CO_2 and other greenhouse gases is the modeling of global climate change and its effects on biota. To meet this challenge, global models of atmospheric, hydrologic, oceanic, and terrestrial and aquatic ecological processes need to be improved and coupled so that linkages and feedbacks can be realistically simulated. This project focuses on the weakest component: terrestrial ecosystem models. Efforts to date to combine and extend ecosystem models over global scales have been very limited, partially because the models are developed by ecologists with different research specialties and are often controversial. Nevertheless, global terrestrial ecosystem models are necessary to describe – in terms of surface energy balance, hydrological balance, and the carbon cycle – interactions between the atmosphere and biota over periods of decades and longer. With the improvements in climate models and computer capabilities that will occur in the 1990s as a result of efforts such as DOE's Atmospheric Radiation Measurement (ARM) and Computer Hardware, Advanced Mathematics, and Model Physics (CHAMMP) programs, the opportunity exists to begin complementary work on global terrestrial ecosystem models.

Mathematical and theoretical analyses of terrestrial ecosystems on a landscape scale are emphasized in this work. Mathematical methods are used to describe spatial patterns of surface vegetative species, surface biophysical properties, and terrain. Terrestrial ecosystems are aggregated and analyzed so that useful parameterizations can be derived to model the responses

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* This project is closely related to a broader, more general companion LDRD project entitled "Modeling and Remote Sensing of Global Terrestrial Ecosystems."

– and the associated feedback – of biota to climate change. The models may be coupled to atmospheric general circulation models to facilitate the description of biotic reactions to climate change.

Fractal analysis is used to evaluate data and to model surface conditions. Topological analyses of spatial data are conducted. Improved indices of landscape habitat diversity are developed. Such techniques lead to methods that can mathematically aggregate surface properties on a landscape scale so that parameterizations can be developed for use in large-scale numerical models.

Technical Progress and Results: Progress was made in developing spatial analysis tools and conducting spatial analyses of vegetation data. A standing problem has been that tools for analyzing spatial data have not been available or have had serious limitations (e.g., semivariance analysis is prone to artifacts). A method developed for describing strange attractors was usefully adapted to the analysis of spatial features of landscapes. This method is the information dimension, which quantifies the spatial variation in the frequency with which a function visits regions of space. For vegetation, the function is a similarity measure for stands of vegetation, normalized for the total area of the map. Software was written to compute the information dimension, and vegetation data were analyzed for a test case.

Statistical aspects of estimating spatial features were also explored. Fractal measures were found to have generally been treated in a statistical vacuum, whereas confidence limits around these estimates do in fact need to be considered. Examination of the use of transects to obtain estimates of surface (e.g., topography) properties demonstrated that transects as samples of the surface can exhibit extreme variability. Conditions for extrapolation of transect data to surfaces or volumes were determined. A manuscript reporting this work has been submitted.

To interface general circulation models and surface models such as the biosphere-atmosphere transfer scheme (BATS), many land cover types must be aggregated into fewer types because the computational load of the full resolution of land types is overwhelming. Currently this aggregation is based on similarity of types. A new method based on dynamic similarity was developed. In this new method, the results obtained by running a surface energy and water exchange model such as BATS for the multiple types within a region are used as input to reparameterize BATS and find a single new cover type that has the same dynamic behavior as the aggregate of all the cover types actually occurring in the region. This single new cover type is then used for the dynamic simulation of global climate over long time periods. To implement this approach, BATS was tested for its parameterizability. The results showed that BATS is not easy to parameterize uniquely. That is, after a small perturbation to the parameters for a cover type, it is difficult to recover the true parameter set by fitting BATS to the sample output from the true model. A new version of BATS is under development at NASA, and when this version is available the method may be tried again.

Proposals for program support have been directed to USDOE/OHER and USEPA.

Specific Accomplishments:

Publications:

Loehle, C., and G. Wein. "Landscape Habitat Diversity, an Information Theoretic Measure." Draft manuscript being revised for resubmission to *Ecology*.

Loehle, C., "Estimation of Fractal Dimensions from Transect Data." Submitted to *Ecology*.

Presentations:

Loehle, C. "Landscape Habitat Diversity." U.S. Forest Service Laboratory, 17 July 1992, St. Paul, MN.

Loehle, C. "Landscape Habitat Diversity, an Information Theoretic Measure." Annual Meeting, Ecological Society of America, 10 August 1993, Honolulu, HI.

92-181 -- MESOSCALE STUDIES OF GLOBAL CLIMATE CHANGE

Associate Laboratory Director Area: Energy, Environmental, and Biological Research

Principal Investigator: Ruth A. Reck, Environmental Research Division

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$ 65K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: To initiate a global climate change program that differentiates the importance of various spatial (largely regional) and temporal scales in the consideration of climate change processes, impacts, and strategies.

Approach: Considerable research is being conducted at Argonne in the area of global climate change. This research includes (1) development of computational techniques to model climate change (CHAMMP), (2) development of measurements to improve climate models (ARM/CART), (3) the consideration of macroeconomic models for the determination of societal and environmental impacts, and (4) the consideration and development of energy systems technology and policy for energy response strategies. For the country, it is especially important that Argonne's background in regional and microscale systems be applied to the global problems of emissions trends, climate response, and the likely role of proposed fossil fuel mixes over the next century. Argonne's research relevant to global climate change includes the following:

- Atmospheric and geophysical sciences
- Terrestrial and aquatic ecosystems
- Energy and environmental policy
- Advanced energy systems
- Control/remediation of greenhouse gas emissions and pollutants
- Supercomputing capabilities to manage very large data systems
- Medical research
- Macroeconomic analysis to study the implications of carbon dioxide policies

Improved methods are needed for understanding the importance of scale in predictions of global change and for accurately detecting changes that might occur. By using innovative modeling approaches and by partitioning global-scale data, research relating to the spatial and temporal scales of climate change will be initiated in three basic areas: climate processes, societal and environmental impacts, and response strategies and assessment. Examples of projects to be initiated include the following:

- The embedding of a mesoscale model within a general circulation model of the atmosphere.
- Scaling of greenhouse gas source and sink terms within a general circulation model.
- The scaling of future health effects on the basis of calculated regional changes in physical variables.
- Regional response strategies and technology transfer for global climate change.

Technical Progress and Results:

Work was initiated in June 1992, and the results reported here represent four months of work. Effort was directed toward organizing and defining objectives and future goals of the Argonne Global Climate Change Program and establishing the necessary support staff required to implement the program. Because of the diversity in global climate programs within Argonne and their dispersion throughout the Laboratory's organizational structure, much effort was spent in identifying and understanding the goals of these programs. To assist in achieving this goal, an internal workshop on regional-global interactions in climate change modeling was held on August 14, 1992. This workshop provided an opportunity for Argonne scientists to present the status and results of their global climate programs. Program staff also participated in a two-day workshop on "The Earth's Climate as a Dynamical System", held at Argonne on September 25 and 26, 1992. The workshop was intended to stimulate theoretical research in climate dynamics in support of the DOE CHAMMP climate modeling program. Work will continue during FY 1993 to develop a firm research program that translates global scale climate data into regional responses.

Specific Accomplishments:

There are no additional accomplishments beyond those cited above because of the short duration of this program.

92-042 -- DEVELOPMENT OF CAPABILITY TO CHARACTERIZE AND TO STUDY PROPAGATION OF HAZARDOUS WASTE-BEARING COLLOIDS INTO ENVIRONMENT

Associate Laboratory Director Area: Engineering Research

Principal Investigator: J. K. Bates, Chemical Technology

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$121.4K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: The transport of radionuclides and hazardous elements from waste disposal sites depends on whether the elements of interest are dissolved or suspended in solution. Material suspended in solution has different transport characteristics than dissolved material. The purpose of this program was to develop methods to characterize colloidal material (<1 μm in size) as to its composition, form, and radionuclide content and to apply the methods to characterize colloids formed during waste-form reaction. The information regarding colloidal generation will be used to evaluate the importance of colloids as a means of radionuclide transport and will help evaluate the performance of waste forms in disposal settings.

Colloid formation and transport have been identified as an important potential process by which radionuclides may be dispersed from a high-level nuclear waste repository containing glass, spent fuel, or potential IFR waste forms. To fully evaluate the performance of waste in a repository setting, the contribution colloids make to radionuclide dispersal must be established. Prior to this program, no methods existed to isolate and characterize colloids that are produced directly from the waste form. Because of the lack of methods to evaluate colloids, the colloidal contribution to waste-form performance was largely ignored. Since solubility limits were assumed to control the release of transuranic elements and this release was very low in the Yucca Mountain environment, there was no reason to question issues related to spent fuel performance. Thus, a clear need existed to develop methods to characterize colloids.

Approach: The scope of the investigation centered on developing methods to isolate colloids from solution; to characterize their composition, form, and radionuclide content; and to evaluate their potential for transport. We evaluated colloids generated due to the reaction of high-level waste glass and UO_2 and showed the importance of colloid formation compared to other types of radionuclide release.

We pursued three approaches to characterize colloids: (1) sequential filtration, isolation, autoradiography of individual colloids followed by transmission electron microscopy (TEM) investigation; (2) micromanipulation and mounting of colloids directly for sectioning using ultramicroscopy followed by TEM investigation; and (3) characterization of colloids in solution using electrokinetic potential measurements as a function of pH and ionic strength. Each of these is discussed below.

Technical Progress and Results:

(1) Individual particles released to the leachate during the reaction of high-level waste glass were isolated on filters and segregated using small-particle handling procedures developed in this program. Autoradiography indicated a varied distribution of radionuclides between these particles, and TEM was used to characterize the particles. The results showed that the Pu and Am are isolated in discrete colloidal phases.

(2) Individual particles were mounted directly on an epoxy block and subjected to autoradiography. These particles were then sectioned and examined with the TEM. This is an easier method to characterize the particles compared to #1 but is not isotope specific.

(3) Colloidal solutions were evaluated for size distribution and stability as a function of leachate chemistry. It was found that as the ionic strength of the solution increases, the stability of the colloids decreases. Thus, for high-level waste glass extended reaction results in reduced colloid generation.

Based on the information described above, we have developed techniques to isolate and characterize colloids produced due to waste form degradation. These techniques will be applied to ongoing and proposed waste-form testing programs to further characterize waste-form performance.

Specific Accomplishments: Based on the methods developed, we have written proposals to characterize the plutonium-contaminated soils at Johnston Atoll and the uranium-contaminated soils at Fernald, Ohio. The following articles were published or submitted:

"Colloid Formation during Waste Form Reaction: Implications for Nuclear Waste Disposal," Bates, J. K., Bradley, J. P., Teetsov, A., Bradley, C. R., and ten Brink, M., Science , 256 (1992) 649-651.

"Analytical Electron Microscopy Study of Colloids from Nuclear Waste Glass Reaction," Buck, E. C., Bates, J. K., Cunnane, J. C., Ebert, W. L., Feng, X., and Wronkiewicz, D. J., accepted for presentation at the 1992 Fall Materials Research Society Meeting, Boston, MA, November 30-December 4, 1992.

A presentation was made to the National Waste Technical Review Board on methods to characterize colloids generated in waste-form reaction.

92-049 -- LABORATORY-SCALE SIMULATION OF NUCLEAR WASTE PACKAGE PERFORMANCE

Associate Laboratory Director Area: Engineering Research

Principal Investigator: J. K. Bates, Chemical Technology
P. A. Finn, Chemical Technology

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$192.3K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: The purpose is to develop and demonstrate designs for laboratory-scale simulation of radionuclide release scenarios from waste packages under unsaturated conditions, i.e., those anticipated at the potential Yucca Mountain repository. The intent is to develop a laboratory-scale hot-cell testing capability for these simulations. Initial tests of the designs will be developed and conducted for spent nuclear fuel to evaluate its performance under unsaturated conditions. The results, however, will be useful for simulating radionuclide release from other radioactive waste materials buried in an unsaturated media. The results will also be used to evaluate the performance of spent fuel in a repository to be compared with other potential waste disposal options.

Approach: Prediction of long-term radionuclide release performance of high-level nuclear waste packages is based on numerical performance assessment models that will require validation. For validation, laboratory simulation is required since it is not possible to conduct field experiments. Development and testing of suitable designs for conducting these simulations are, therefore, required. No in-service condition tests have been performed or proposed that allow for an evaluation of disposal options or repository design.

Several scenarios have been developed to define the conditions under which radionuclide release might occur from waste packages under unsaturated conditions. These scenarios include exposure of the package to dripping water, hot humid air, and/or an unsaturated rock environment that allows diffusive and convective transport of radionuclides along continuous water films. This effort will simulate radionuclide release from spent fuel under each of these conditions.

The radionuclide release behavior of spent fuel will be monitored with leach tests designed to evaluate the factors affecting performance under unsaturated conditions. Since the kinetics of reaction and radionuclide release are slow, two years of testing will be required to attain enough information to evaluate the utility of the test design and to produce results.

Additional participants in this work include J. C. Hoh, J. W. Emery, and L. D. Hafenrichter, who set up and will monitor the experiments in the Senior Cave of Bldg. 205.

Technical Progress and Results: In FY 1992, a task plan was developed which identified the range of parameters to be examined to simulate each release scenario under unsaturated conditions for spent fuel. This task plan was submitted to the technical project management staff of the Yucca Mountain repository for review. Their recommendation was that it be published and distributed to regulatory agencies.

The design, fabrication, and proof testing of a prototype testing facility in the Senior Cave in Bldg. 205 were completed. Experimental procedures for leach tests with spent fuel under unsaturated conditions were developed and reviewed for quality assurance. A safety review was held for the initiation of the spent fuel leach tests. The leach tests with spent fuel were initiated.

Specific Accomplishments: The task plan, after being reviewed by the project management staff for Yucca Mountain, has been submitted for publication. A program plan and funding schedule to continue and expand the work in FY 1994 were submitted to the Yucca Mountain Project and incorporated into their 2001 planning document. A presentation was scheduled to be made to the Yucca Mountain Project in November 1992 on the status of the tests.

92-053 -- CHEMICALLY BONDED CERAMIC WASTE FORMS

Associate Laboratory Director Area: Engineering Research

Principal Investigators: J.C. Cunnane, Chemical Technology
A.S. Wagh, Materials and Components Technology

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$198.6K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: To show that chemically bonded ceramics (e.g., phosphate - bonded materials) are promising materials for use as waste forms in the disposal of a wide variety of radioactive and mixed wastes. Ideally, a waste form material should stabilize (i.e., convert the waste contaminants into a chemically durable form) and solidify (i.e., convert the waste into a monolithic solid form) the waste. The underlying concept in this project is to use phosphate to mineralize the heavy metal and radioactive constituents of the waste into insoluble phosphates and, at the same time, to bind the mineralized material into a durable monolithic solid form.

The scope of this LDRD project was intended to provide a basis for obtaining future DOE/EM funding for additional development of chemically bonded ceramics as waste form materials.

Approach: Literature information indicates that phosphates may be useful for stabilizing and solidifying a wide variety of radioactive and mixed wastes. Chemically bonded phosphate ceramics are inorganic polymers which solidify at near ambient temperatures. They offer the possibility of forming durable waste forms, while avoiding the problems (e.g., waste volatilization) associated with the high-temperature processing required to make conventional ceramic and glass waste forms. The stability, low solubility, and affinity of phosphate phases to incorporate waste are indicated by observations that secondary actinide phosphate phases are formed when phosphorus-containing borosilicate glass dissolves. The stability and low solubility of heavy element phosphates is also reflected by the interest in use of phosphate phases (e.g., monazite, apatite, and sodium zirconium phosphate) as high-level nuclear waste forms. In addition, the insolubility of phosphate phases and their affinity to incorporate or adsorb a variety of cationic contaminants as solid solutions are illustrated by their use in chemical precipitation and ion exchange. This project involved investigation of magnesium phosphate and aluminum phosphate as candidate waste form materials. Specifically, the project plan involved the following:

1) Development of processes to fabricate low-porosity monolithic specimens of magnesium and aluminum phosphate.

2) Production of test specimens suitable for physical and chemical characterization.

3) Characterization of the physical (porosity and strength) and chemical (mineralogical phases, chemical durability/leaching, and radiation stability) properties of the test specimens.

4) Production of test specimens which incorporate selected radionuclide and heavy metal contaminants, under simulated waste form production conditions, and characterization of the chemical and physical properties of the resulting specimens.

The project was conducted as a cooperative effort between CMT and MCT Divisions. The initial focus was on production and characterization of specimens of magnesium phosphate and aluminum phosphate, and most of this effort in FY 92 was conducted by MCT. This involved process development and testing, porosity measurements, compressive strength measurements, x-ray diffraction to characterize the specimen mineralogy, and sanning electron microscopy to characterize the specimen microstructure. The CMT effort focused on characterization of the chemical and radiation stability of test specimens produced by MCT. It included leach testing (using ANS 16.1, TCLP, and MCC-1 procedures) and determination of the effects of gamma irradiation to an absorbed dose of about 100 MRad.

The individuals who collaborated in this work were D. Singh (MCT) and S. Armstrong and D. Reed (CMT).

Technical Progress and Results: During FY 92, processes were successfully developed for producing low-porosity monolithic specimens of magnesium phosphate and aluminum phosphate. The binding phases were identified, and the compressive strength was determined as a function of residual porosity. Magnesium phosphate was used to encapsulate zeolite as an initial test of the waste loading capacity that may be achieved. The attached figures illustrate the effects of porosity and zeolite loading on the strength of the samples; they indicate that the compressive strength at high zeolite loadings decreases with increasing porosity. Leach testing and initial radiation stability testing indicate that the magnesium phosphate is a durable material.

Specific Accomplishments:

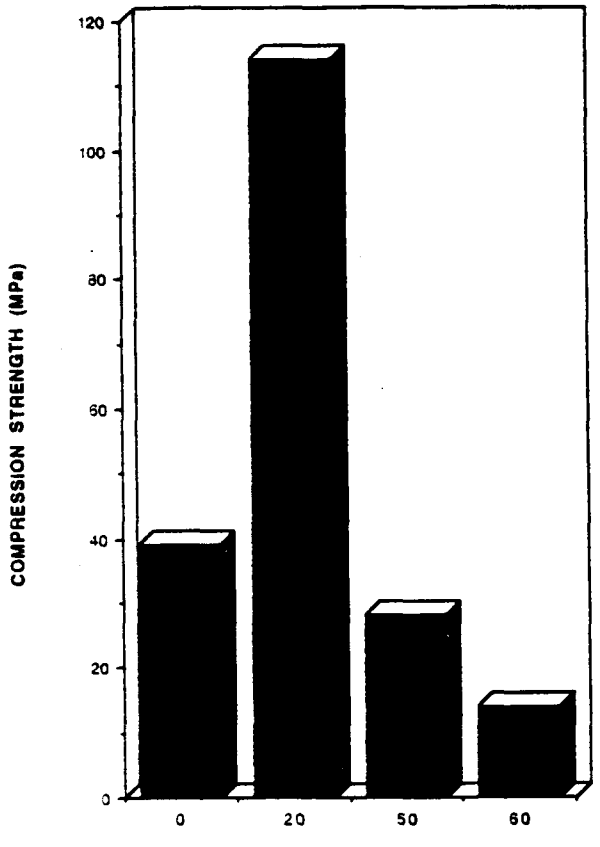
1) A paper on this work has been submitted for presentation at the Waste Management 93 Conference.

2) Two proposals (Technical Task Plans) have been submitted in pursuit of funding from DOE/EM for continuation of this work.

3) Chemically bonded ceramics are identified as a candidate waste form for mixed waste solidification in a status report for low-level mixed-waste waste forms that is being prepared for the DOE/EM Mixed Waste Program.

4) As a spinoff from the project, magnesium phosphate has been identified as a material that may be useful as a high-temperature binder and sealant in fuel cell applications. Detailed investigations and development for this application have been initiated as part of the Solid Oxide Fuel Cell Development Program.

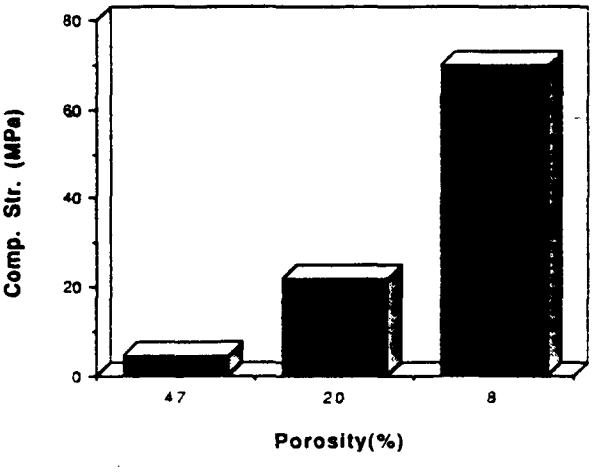
Figure: The variation of the strength of magnesium phosphate with zeolite loading is shown in A. B and C are SEM micrographs of fracture surfaces of magnesium phosphate loaded with 20% and 50% zeolite, respectively. They show that the porosity increases significantly with zeolite loading. The compressive strength at high zeolite loading is correlated with the porosity in D.



A.

B.

C.



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92-168 -- FUNDAMENTAL CHEMISTRY OF CLAYS - TOXIC CHEMICAL INTERACTIONS ELUCIDATED BY SYNCHROTRON RADIATION TECHNIQUES

Associate Laboratory Director Area: Physical Research

Principal Investigator: S. R. Wasserman, Chemistry
K. A. Carrado, Chemistry
R. E. Winans, Chemistry

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$125.6K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: The objective of this study is to explore the fundamental chemistry of clays at the atomic and molecular level. An understanding of the interaction of organic and inorganic materials with clays will aid in the development of new approaches for the solution of problems in environmental restoration.

Approach: The Department of Energy has stated in recent reports that creative and innovative research on clays is required to define their fundamental characteristics and their interactions with organic and inorganic hazardous wastes. Clays are ubiquitous constituents of the earth. In addition to their prevalence in nature, they play vital roles in industry as absorbents, catalysts, and barriers for the transformation and migration of organic and inorganic matter.

Although they have been studied extensively, many fundamental issues involving clays remain unsolved. Their extended, layered structure, lack of long-range order, and ionic nature present a major challenge to experimental and theoretical analysis. Synchrotron-based X-ray methods offer a hope of overcoming the current deficiencies in the characterization of clays. Because a knowledge of these materials and their interactions with other ions and molecules is of extreme practical importance in areas such as toxic waste migration, we have examined the short-range (1-5 Å) structure of clays. In addition to elaborating the molecular structure of clays, we have attempted to define the reaction pathways within the reactive environment provided by these structures. This knowledge is vital for subsequent advances by other research and development teams, whose work depends upon a firm understanding of the chemistry of clays in the environment. Much of this work is pioneering in the sense that the experimental approaches differ markedly from prior strategies.

Because of the complexity of a clay's structure, this program has required a multi-disciplinary approach to probe the active sites of clays and the chemical and structural changes that occur as reactions proceed within a clay. Currently, our investigations have focused on two complementary synchrotron X-ray methods. The first, X-ray absorption spectroscopy (XAS) has been used to examine the local coordination geometry about transition metal atoms that are present in the clay. The second, anomalous small angle X-ray scattering (ASAXS), provides

information on the distribution of a specific metal within a clay. The latter experiments are at best preliminary in scope. The X-ray intensities required for ASAXS studies are at the very limits of current synchrotrons. Definitive experiments will have to await the start-up of the Advanced Photon Source.

Technical Progress: The use of X-ray based analytical methods for the study of clays often requires the introduction of a suitable probe cation into the active region of a clay. Clay materials containing Cu and Ni cations were prepared by ion-exchange methods for X-ray absorption studies. Both these metals are common in the environment and can be easily utilized for XAS studies. The XAS experiments on Cu-clays have been completed. These investigations have shown that, as protic solvents enter a clay, the coordination structure about the copper ion changes from a square planar arrangement to a distorted octahedron. In addition, the distance from the copper atoms to its nearest neighbors increases on the order of approximately 0.03 Å. Figure 1 presents the typical changes in the X-ray absorption spectra, both near-edge (XANES) and extended fine structure (EXAFS), for Cu-clays as the liquid penetrates into the material. Table 1 lists the fitting parameters (number of nearest neighbors, n, bond distance, r, and disorder, $\Delta\sigma^2$) which describe the environment about the Cu atom. These parameters, which are derived from the EXAFS spectra, demonstrate that expansion of radial distance occurs for each solvent which was examined. Comparison of the local structure around the cupric ion with those of Cu ions in aqueous solution indicates that the local environment created by the clay and the solvent is essentially equivalent to a solution. These experiments represent the first observation by EXAFS of a change in bond distance as a coordinated species changes from a solvated solid to a dissolved cation.

The interpretation of X-ray absorption spectra requires a number of mathematical manipulations. As part of this project, a new software analysis package has been developed for this purpose. The new software offers increased flexibility and is currently portable onto most computer platforms present within the Chemistry division.

Specific Accomplishments: This LDRD project supported experiments at the National Synchrotron Light Source and the Stanford Synchrotron Radiation Laboratory. The funds also provided for consultations with Dr. Farrel W. Lytle of the EXAFS Company, Seattle, WA.

Papers and presentations arising from this project include:

Carrado, K. A.; Wasserman, S. R. "An X-ray Absorption Study of the Solvated Cu(II) Ion: Transition from a Solvated Solid to the Dissolved State", *Journal of the American Chemical Society*, submitted.

Wasserman, S. R. "X-ray Absorption Spectroscopy of Copper-Clays", Clay Minerals Society, Minneapolis, MN, November 4, 1992.

Wasserman, S. R. "The Use of X-ray Absorption Spectroscopy for the Analysis of Clays: Fundamental Studies Related to Environmental Restoration", Amoco Oil Company, Naperville, IL, May 26, 1992.

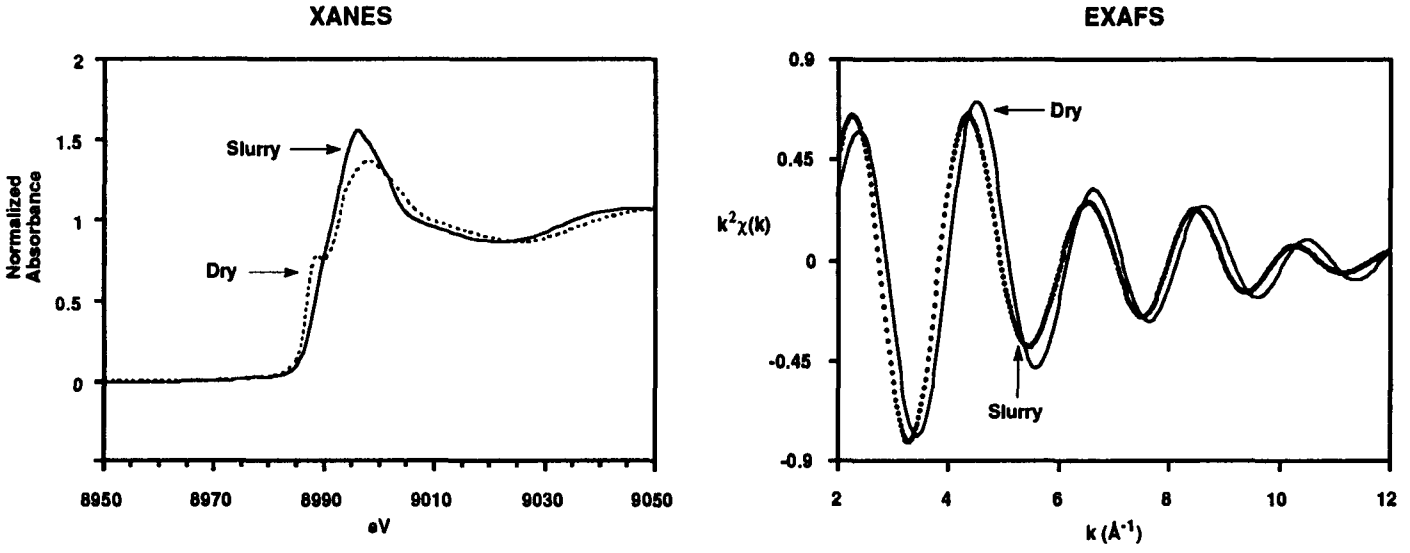


Figure 1

a) X-ray Absorption Near Edge Spectra (XANES) of Cu(II) in bentonite: air-dried powder and slurry in water.

b) Fourier-filtered EXAFS spectra of the first coordination sphere of Cu(II) in bentonite: air-dried powder and slurry in water.

Table I. Summary of Fitting Parameters for the EXAFS Spectra of Cu-Bentonite in Protic Solvents[a,b]

	Powder			Slurry		
Solvent	n	r	$\Delta\sigma^2$	n	r	$\Delta\sigma^2$
Methanol	4.0	1.93	0	4.3	1.96	.0025
Ethanol	3.9	1.93	-.0002	4.2	1.96	.0010
Water	3.9	1.92	-.0002	4.1	1.95	.0006
Ethylene Glycol	3.7	1.93	.0003	3.9	1.96	.0009

[a]n = number of neighboring atoms; r = radial distance between absorbing and backscattering atoms; $\Delta\sigma^2$ = difference in Debye-Waller factors between sample and reference.

[b]The values for n and $\Delta\sigma^2$ are referenced to the Cu-Bentonite powder dried from methanol (n=4, $\Delta\sigma^2 = 0$)

92-171 -- ENVIRONMENTAL EFFECTS OF REMEDIATION AND RESTORATION ACTIVITIES IN AQUATIC SYSTEMS

Associate Laboratory Director Area: Energy, Environmental, and Biological Research

Principal Investigator: E.A. Stull, Environmental Assessment and Information Sciences

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$ 16.2K
FY 1993	$ 28K
FY 1994	$ 0K

Purpose: The environmental effects of energy-development-related remediation and restoration activities on ponds and wetlands are being investigated. Remediation and restoration of these ecological systems occur at both ends of energy development projects: construction and cleanup. Regulations require that planning for and implementation of such activities include consideration of wetland protection, mitigation of wetland losses, and the ecological effects of habitat alteration. Published research has emphasized the effects of remediation and restoration activities on rooted wetland vegetation. The purpose of the research reported here is to provide comparable information on the limnetic (open water) habitats of ponds and wetlands.

Approach: This study involves review of the literature on aquatic effects, evaluation of past and current remediation and restoration activities, field investigations of natural and mitigated or restored wetlands, and preparation of publications in this technical area. Summary of past and current activities involves review of literature in scientific and applied technology fields, review of agency reports, and interview of personnel from organizations conducting aquatic remediation and restoration activities. The field investigations are conducted on several local water bodies that have been, or are candidates for, mitigation, remediation, or restoration activities. Investigations include comparisons of aquatic biota and physical and chemical characteristics of both managed and unmanaged wetland ponds. Publications in preparation include technical memoranda and journal articles.

Technical Progress and Results: This project began in FY 1992. Field investigations were carried out at a wetland re-created as mitigation for wetland losses from construction of the Advanced Photon Source (APS). The field work included weekly measurements of water temperature, oxygen, pH, phytoplankton abundance, zooplankton composition, and aquatic plant distribution. For comparison purposes, similar data were obtained for the Ecology Area Pond, an undisturbed wetland that is similar to the type of wetland destroyed and re-created at the APS site. These measurements indicated significant differences in temperature, oxygen concentration, and pH between the re-created and pre-existing ponds. The water of the APS pond was warmer, more basic in pH, and supersaturated with oxygen. The water of the Ecology Area Pond was cooler, of nearly neutral pH, and low in oxygen content. In both

ponds phytoplankton abundance was low, and zooplankton abundance was high and of similar taxonomic composition. Mayflies were present in net samples in the APS pond, where oxygen was high; but tube-dwelling annelid worms of uncertain taxonomy were abundant in the Ecology Area Pond, where oxygen concentrations were low. Assisting in field investigations were J. Dundek (Teacher Research Associates Summer Appointment) and R. Van Lonkhuyzen, EID.

Nearly all wetland areas and ponds on Argonne National Laboratory develop dense algal mats on the water surface during late spring and early summer. Investigations of these mats indicated the presence of several genera and many morphological types of algae belonging to the family *Zygnemataceae*. Such high biodiversity was unexpected and is believed to be unique for floating algal mats. Biodiversity studies were performed at three local ponds: Ecology Area Pond at ANL, Kearney Road Ponds at ANL, and the Sag Quarries at the Palos Forest Preserve. Over 15 other sites were more casually studied. Results indicate that mats formed of the alga genus *Spirogyra* contain many morphotypes (high diversity) that are evenly distributed throughout the algal mat (high similarity) at distance scales of 1 mm to 100 m. Trends in biodiversity among water bodies appears to be related to size of the water bodies and the genera of algae present. Dr. R.M. McCourt (DePaul University) and Dr. R.W. Hoshaw (University of Arizona) reviewed the data and recommended publication. Dr. Mathew Liebold (University of Chicago) began work on similar communities composed of *Lemna* (duckweed).

Specific Accomplishments: During FY 1992 the review of pertinent literature was partially completed and preparation of the following articles or reports was initiated:

"Biodiversity of Zygmenatacean Mats," E.A. Stull and R.M. McCourt, for submittal to Journal of Phycology.

"Limnology and Ecology of a Recreated Wetland Pond," E.A. Stull, K. LaGory, J. Dundek, and R. Van Lonkhuyzen, for submittal to an appropriate journal.

"Aquatic Effects of Wetland Remediation, Restoration, and Reconstruction," E.A. Stull, for submittal as an ANL Technical Memorandum.

92-175 -- UNVENTED THERMAL PROCESS FOR TREATMENT OF ANL MIXED WASTE

Associate Laboratory Director Area: Engineering Research

Principal Investigator P. A. Nelson, Chemical Technology
W. M. Swift, Chemical Technology

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$106.1K
FY 1993	$200K
FY 1994	$200K

Purpose: The purpose of this project is to demonstrate the feasibility of a new concept for destroying organic materials contained in mixed waste in a process that does not release gaseous products of combustion to the environment. Part of the effort will be directed to providing an experimental facility which will be used to process up to 200 L of ANL organic mixed waste (such as scintillation-counting waste) and, thus, contribute to the disposal of a backlog of mixed waste. This facility will also be available for experiments with mixed waste or their simulations from other sites. Thus, this project will assist in obtaining funding for such efforts and in further establishing a program on waste management at ANL.

Approach: An existing 15-cm (6-in.) diameter fluidized-bed reactor, which has been used for experiments on fluidized-bed burning of coal, is being converted for use in destroying organic waste material. In this process, the reaction product gases are removed from the fluidizing gas by reaction with lime and condensation of water, and the remaining gas is recirculated with oxygen addition to support the reaction. Preliminary revisions of the reactor will soon be completed, and a few runs will be made without gas recirculation to establish appropriate operating conditions. Design work is under way, and parts are being ordered for additional modifications which will include installation of a recirculation loop, including a condenser, blower, and oxygen supply apparatus. Instrumentation, waste water collection, and waste gas storage apparatus will also be provided. Most of the modifications were completed in FY 1992, and testing of the unit as an unvented reactor will be carried out in FY 1993.

Organic waste treatment systems that are reported in the literature have in common the disadvantage of continuously releasing gaseous products from an exhaust treatment system. Achieving high conversion efficiencies requires long steady runs under constant feed conditions. That requirement is difficult to meet in treating the small batches of organic mixed waste stored at ANL. These processes release tritium with the water vapor. It is expected that there would be considerable local community opposition to an EPA permit for any conventional incineration system if used for treating mixed waste at the ANL site. The release of gaseous products, which may contain hazardous materials, is the main shortcoming of incinerators. Oxidation processes for destruction of organic and biological materials are otherwise considered favorably by environmentalists because these processes eliminate the waste and, thus, avoid future problems associated with storage or burial.

A design has been developed for processing organic mixed waste in a system that does not release gases during the thermal treatment operation. The main unit in this process is a fluidized-bed reactor containing a bed of calcined limestone (CaO), which reacts with gases given off during oxidation of organic materials. Gases that will react with CaO include CO_2, SO_2, HCl, HBr, and other acid gases. Water vapor formed during the oxidation process is carried off with the fluidizing gas and removed in a condenser. Oxygen is added to the remaining gas, which is recirculated to the reactor. Thus, for most organic waste materials there is no net production of gas by the reactions going on within the equipment, although small amounts of nitrogen might need to be collected and stored during the destruction of some organic compounds, such as amines. The organic material to be treated is continuously fed into the fluidized bed as a liquid, and the bed material (CaO) is also continuously fed and continuously withdrawn through an overflow pipe.

This process is ideally suited for the small quantities of many types of mixed wastes in the ANL inventory. It is especially suited for the most voluminous waste now on hand, which is scintillation-counting fluid having a toluene base.

The waste materials from the process, the spent lime from the bed and water from the condenser, would be combined with other cement-making materials to produce a cement which would be stored in barrels for disposal at a low-level waste site. This initial effort on process development does not involve the cement-making part of the process, only the treatment of organic waste in the reactor.

Later work could involve the development of a head-end treatment process for the large volume of scintillation waste, which is contained in 200 drums of 55-gal capacity. Each drum holds 2000 to 4000 vials of toluene-based scintillation fluid, usually containing radioactive materials. The vials are packed in vermiculite, which also must be treated as a mixed waste. With the proper head-end step to separate the organic liquid from the balance of the materials, this waste inventory could be processed by the basic technique proposed herein. Also, extensive biological mixed wastes at ANL could be treated by the proposed reactor process for destruction of the biological materials. Biological wastes, such as dead animals, would require a separate burning unit. The gases from that unit would be directed to a fluidized bed of lime and then recirculated to the burning unit.

Technical Progress and Results: A 15-cm (6-in.) diameter fluidized-bed coal combustor is being modified to demonstrate the concept of destroying organic waste material without a net production of gaseous products. For its use as a coal combustor, the reactor was equipped with an air compressor for supplying air for fluidizing the bed and burning the coal, and the exhaust was vented. Apparatus for continuously feeding and withdrawing bed material was already available as part of the original coal combustor.

In a preliminary modification of the equipment, to be completed in October, a nozzle is being installed for direct injection of scintillation counting fluid. Preliminary experiments, which are expected to be completed before the end of CY 1992, will help to establish operating conditions and demonstrate the rate of CO_2 reaction with the lime bed. Another important feature of the preliminary experiments is to demonstrate that essentially no unreacted organic

material is removed with the lime bed, even during continuous withdrawal of the bed material.

A National Environmental Policy Act (NEPA) Environmental Evaluation Notification Form (EENF) was completed and submitted to the ANL Environment, Safety and Health/Quality Assurance Oversight (EQO) office. Approval to proceed with the experimental work has been granted pending a safety review.

Work has also been done on preparing for more extensive modifications of the unit and on ordering the equipment needed for these modifications. The new equipment would include: (1) a particle filter section to be operated in the hot zone above the fluidized bed, (2) a water condenser, (3) a circulating blower, (4) an oxygen supply system, (5) water-waste and gas-waste storage systems, and (6) appropriate piping and instrumentation. The design, ordering, and partial installation of these items will continue through the end of CY 1992.

A computer program has been developed for determining the optimum operating conditions for the unit and for sizing the condenser and flow equipment that are now on order. This program will also be used for designing future equipment for operating with radioactive material. The program carries out energy and material balances and assists in determining optimum conditions. As a result of a preliminary analysis, it has been concluded that the reactor will operate efficiently at slightly below atmospheric pressures; this provides the safety feature that all leaks result in air being drawn into the system rather than toxic materials leaking out. Very high throughputs can be achieved by providing a water-cooled heat exchanger inside the reactor. Such a heat exchanger having approximately 25 ft (7.6 m) of tubing already exists in the present reactor.

Specific Accomplishments: Based on the feasibility of the approach demonstrated by the computer analysis, a proposal has been submitted to DOE for revision of the facilities in Building 306 to include facilities for mixed waste treatment involving the unvented reactor concept. A proposal will be submitted to DOE for support of R&D on the process. Materials in support of an invention disclosure have been submitted to the ANL Legal Department.

92-011 -- THEORETICAL STUDIES OF THE PHYSICAL AND CHEMICAL PROPERTIES OF SMALL CARBON CLUSTERS

Associate Laboratory Director Area: Physical Research

Principal Investigator: Robert Harrison, Chemistry
Albert Wagner, Chemistry

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$ 70.8K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: The initial purpose was to develop and apply electronic structure codes for the study small carbon clusters. Clusters of 2 to 18 carbon atoms were envisioned and thus the chemistry of carbon clusters below "bucky ball" size would be explored. Originally the work was to be done in concert with an experimental program but this program was discontinued for lack of funding. As a consequence, the theoretical effort emphasized the development of the necessary codes over applications.

Approach: The calculation of the electronic structure of carbon clusters is a computer intensive problem. While we have efficient codes on serial computers and on modestly parallel computers, no appropriate codes were available on large, massively parallel computers. An example of such a computer and one we have access to is the Touchstone Delta computer at California Institute of Technology. The scope of the carbon cluster problem necessitates electronic structure codes capable of running on a machine of this size (~500 processors, ~8 GB distributed memory). Consequently, the effort of this proposal was directed at developing electronic structure codes that ran efficiently on this computer. In particular, a full configuration interaction (full-CI) code was selected for adaptation to this computer. This code is not only useful for carbon cluster applications but provides a training ground for adapting other more complex codes to massively parallel computers. This in turn benefits laboratory initiatives in high performance computing.

Technical Progress and Results: A full-CI program for the Touchstone Delta was successfully developed by this effort. The code is written in C, is fully scalable to the number of processors, can be efficiently executed on both distributed and shared memory computers (by the use of message passing techniques), and is portable to a wide variety of high performance computers, both serial and parallel.

The full-CI technique involves an iterative solution to a partial differential eigenvalue equation for the electronic wavefunction. This equation is reduced to a matrix algebra

problem by a basis set representation of the wavefunction. The full-CI approach is unique in that the only approximation in the method is the truncation of the, in principle, infinite basis set expansion.

The primary mathematical operation in a full-CI calculation is the determination of a final vector (wavefunction) from an initial (trial) vector via a sparse matrix-vector multiplication. This calculation can easily involve billions of elements and requires the storage of two vectors (final plus initial) of substantial size. We have used the sparsity of the matrix and quantum mechanical identities to reduce the original matrix-vector multiplication to a series of smaller dense matrix-matrix multiplications. In addition, the form of this matrix-matrix multiplication allows us to distribute blocks of independent tasks over all available processors of a parallel computer. We also distribute the large final and initial (or trial) vectors, plus an intermediate vector, over all processors. The resulting code allows us to perform scalable, fully-parallel full-CI calculations with no intermediate disk I/O and relatively little inter-processor communications. Generally, as a block of the matrix-matrix multiplication is being carried out, a gather operation is invoked to collect the necessary vector elements. Once the multiplication is complete, the results are scattered back to the appropriate final vector locations in different processors.

The original sparse matrix-vector multiplication is part of an iterative diagonalization process which can be accelerated by including past vectors in the solution space. We have implemented a modified Davidson algorithm that uses only the current and two past vectors and Lossy compression to accelerate convergence. All three vectors are distributed onto the processors to eliminate disk I/O. In this form, the code can handle a full-CI problem with up to 100 million configurations without disk I/O. Test calculations with this program set a world's record on the number of configurations (95 million) used in a full-CI calculation.

Specific Accomplishments: The code received honorable mention in a national award sponsored by Intel Corporation for the most significant application in high performance computing. This code was used in part to demonstrate our capabilities in high performance computing and contributed to the DOE funding of the High Performance Computer and Communications Initiative entitled *High Performance Computational Chemistry: Scalable Algorithms for Grand Challenges.*

Publications include:

Massively Parallel Full Configuration Interaction Benchmark Electronic Structure Calculations on the Intel Touchstone Delta," Harrison, R. J., and Stahlberg, E. A., *J. Parallel Distributed Computing* (in press).

92-046 -- UNSTEADY FLOW THEORY FOR FLUIDELASTIC INSTABILITY OF TUBE ARRAYS IN CROSSFLOW

Associate Laboratory Director Area: Engineering Research

Principal Investigator: S. S. Chen, Materials & Components Technology

Funding Profile:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$192.5K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: Tube arrays subjected to crossflow are found in process heat exchangers, steam generators, boilers, condensers, and similar equipment. At the present time, development of a reliable theory for predicting instability thresholds is not possible without the key elements, i.e., the motion-dependent fluid forces. The purpose of this project is to develop and apply a methodology for measuring these motion-dependent fluid forces and to complete the unsteady flow theory of fluidelastic instability of tube arrays in crossflow. As a result of this program, three specific goals will be achieved: (1) answers, for which many experts in the world are looking, will be provided for the fundamental questions relating to fluidelastic instability of tube arrays in crossflow; (2) the foundation will be established for the unsteady flow theory of fluidelastic instability of tube arrays and the determination of the applicable ranges of quasistatic and quasisteady flow theories; and (3) a new design guide will be developed and will be a substantial improvement over such existing guidelines as the ASME Boiler code, Section III, Appendix N; and the Standards of the Tubular Exchanger Manufacturers Association.

Approach: A group of tubes submerged in crossflow has the potential to experience dynamic instability. If a system consisting of a tube array in crossflow is operated at a flow velocity above the critical value for instability, severe damage to the tubes is likely to occur, often after only a short period of operation. Since the early 1970s, extensive studies of fluidelastic instability have been reported. Nevertheless, fluidelastic instability remains one of the most debated and complex topics in the area of fluid/structure interaction. Various simplified design techniques have been developed to avoid fluidelastic instability problems in specific applications. However, there remains an urgent need to develop a comprehensive fluid-force-coefficient data base that can be applied to general cases. Without the benefit of such a generally applicable data base, many tube-bundle failures have occurred, some with potential safety hazards and all with significant economic losses.

A systematic, integrated experimental/analytical approach is being followed to study this important and complex problem. In the theoretical aspect, various theories of fluidelastic instability were evaluated and an unsteady flow theory has been developed. The key elements required of the theory were identified and a technique to obtain these elements was developed. In the experimental aspect, the existing flow-induced-vibration test facilities of MCT were employed to establish the necessary experimental setup; the ready availability of existing facilities allows the maximum benefits to be derived from the program. A row of tubes was tested to verify the reliability of the test setup. Once the measurement technique had been established and verified, the following steps were taken:

- The fluid forces acting on tube arrays in crossflow due to the motion of a tube within the tube array are measured and, from the measured fluid forces, fluid damping and fluid stiffness associated with coupled tube motion are calculated.

- Based on the measured motion-dependent fluid-forces coefficients, the stability of tube arrays are analyzed according to the unsteady flow theory.

- A design guide will be developed to predict fluidelastic instability of tube arrays in crossflow, with general applicability to steam generators, heat exchangers, and other mechanical components.

Activities in FY 1992 focused on development and verification of the measurement technique and the acquistion of data from a tube row. The experimental data and unsteady flow theory will be used to develop an improved design guide with general applicability in analyzing fluidelastic instability of tube arrays.

In addition to the principal investigator, program participants include S. Zhu, R. K. Smith, and J. A. Jendrzejczyk.

Technical Progress and Results: Accomplishments in FY 1992 include the following:

- The experimental setup was established using the existing flow-induced-vibration test facilities of MCT, including water channel, force transducers, electrodynamic vibration exciter, and data acquisition and analysis equipment.

- The fluid forces acting on a tube row in crossflow were measured, and the effect of various parameters (including flow velocity, oscillation frequency, and tube oscillation amplitude) were investigated.

- Coupling matrices for fluid damping and stiffness were calculated to correlate fluid forces and tube displacements; see Fig. 1. The calculations were based on measured fluid-force data, and used the potential flow theory to account for the fluid inertial effect. These fluid-force coefficients are functions of reduced flow velocity and other system parameters.

- The stability of tube arrays was analyzed on the basis of the unsteady flow theory, with the use of the measured motion-dependent fluid force data. Once the coupling matrices are known, the unsteady flow theory can be applied in the analysis of various tube arrays.

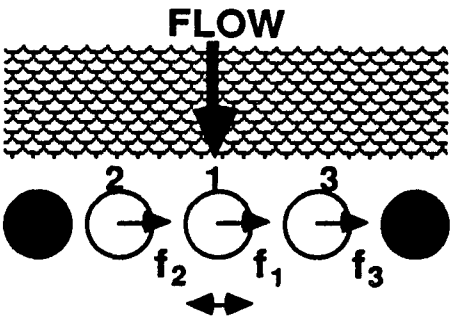
Specific Accomplishments: A reliable general theory of fluidelastic instability of tube arrays in crossflow has been established, and an experimental technique to obtain the motion-dependent fluid forces has been demonstrated. The developed measurement technique has been proposed for other applications, including the dynamic response and stability high-speed maglev vehicles resulting from vehicle and guideway interaction.

The Taiwan Power Company of Taiwan has signed a contract (ANL Contract No. 85540) to provide follow on funding for this project in the amount of $110K for FYs 1993 and 1994.

A meeting was scheduled for November 1992 to discuss, with experts from Japan and France, the possible establishment of an international program on flow-induced vibration.

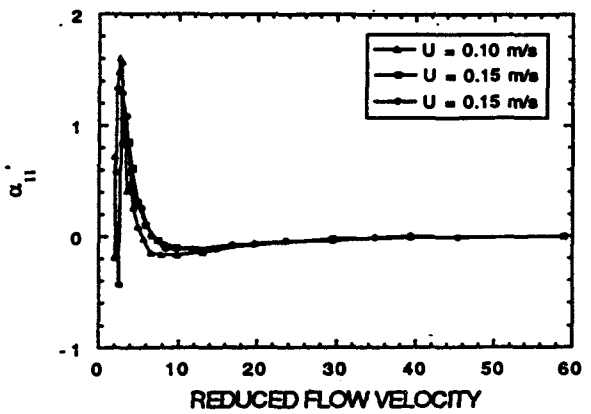
Publications include: "Unsteady Flow Theory for Fluidelastic Instability of Tube Arrays in Crossflow," by S. S. Chen, S. Zhu, and J. A. Jendrzejczyk, ANL Report (draft completed).

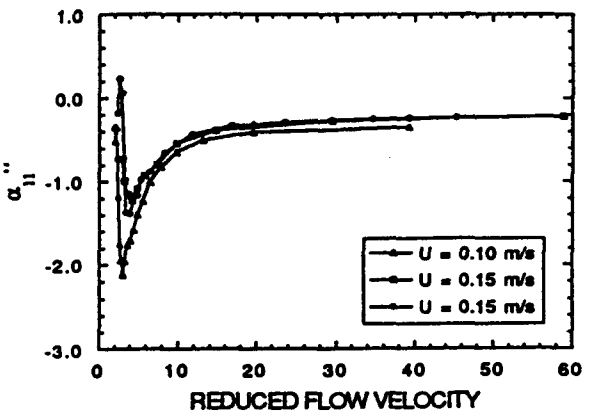
FIG. 1. FLUID-DAMPING AND FLUID-STIFFNESS COEFFICIENTS AS A FUNCTION OF REDUCED FLOW VELOCITY

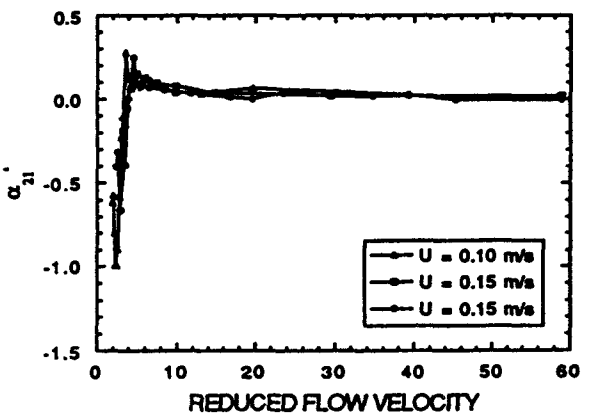


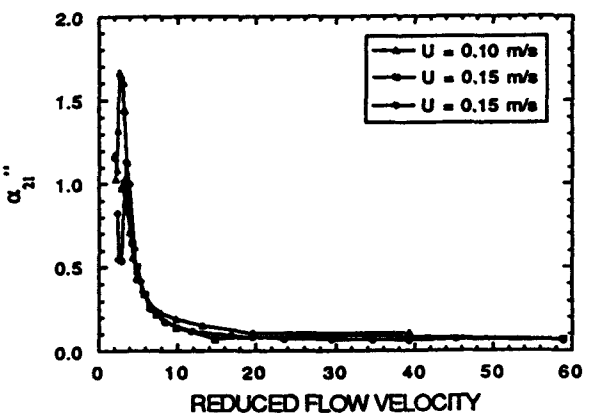
FLUI-DAMPING COEFFICIENTS

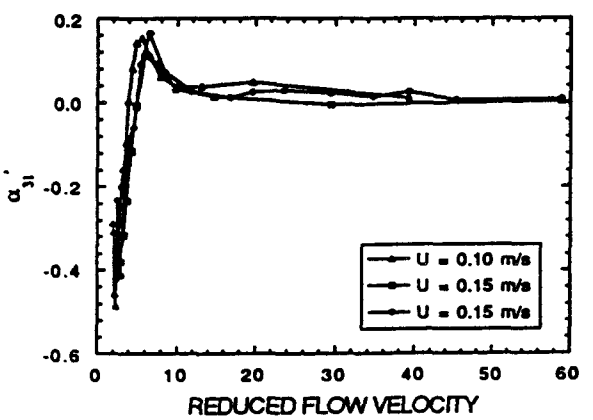
FLUID-STIFFNESS COEFFICIENTS

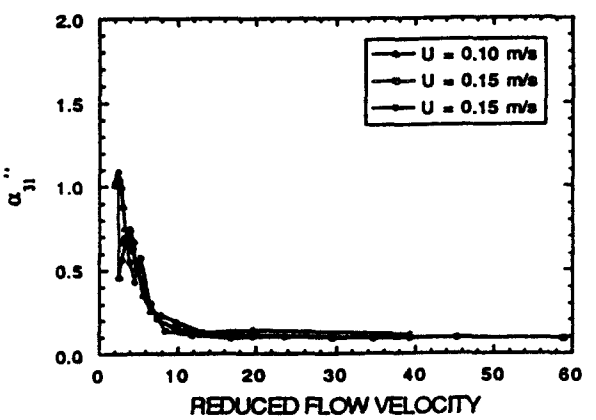












92-165 -- FLOW AND HEAT TRANSFER IN MICROCHANNELED STRUCTURES

Associate Laboratory Director Area: Advanced Photon Source

Principal Investigators:
S. U. Choi, Materials and Components Technology
J. A. Jendrzejczyk, Materials and Components Technology

Funding History:

FY 1990	$ 0K
FY 1991	$ 0K
FY 1992	$ 72.5K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: The objectives of this work are to (1) explore the potential for cooling high-heat-load silicon crystals by liquid nitrogen flow and heat transfer through microchanneled structures (characteristic dimension <0.1 mm), and (2) develop and apply a methodology for characterizing the flow-induced vibration response of microchannel heat exchangers and designing to minimize such response. In addition to directly contributing to the success of the APS project, this project is expected to result in a number of new programs, including the development of advanced cooling technologies for high-temperature superconductors, multichip modules, and fusion reactors.

Approach: The X-ray beams that will be produced by the next generation of synchrotron sources, such as the APS, will be more intense than any available today. Cooling of the first optical element in such intense beams is recognized as a major challenge that must be faced before these very intense beams can be used. Although considerable advances have been made in the art of cooling high-heat-load X-ray optical elements, previous investigations were limited to water-cooled microchannel or liquid-gallium-cooled macrochannel heat exchangers. These investigations showed that major improvements in transferring heat from the surface of the silicon crystal to the cooling fluid were possible. However, in addition to thermal considerations, growing concerns about the effects of flow-induced vibration of the crystal on the quality of the X-ray beam, especially under high-heat-load conditions, are providing a new critical requirement in the design of heat sinks for APS applications. The stringent and contradictory requirements of high heat dissipation and low flow-induced vibration for the APS X-ray monochromators led to the idea of employing laminar flow of liquid nitrogen in microchannels just below the surface of the silicon crystal. This study has two parts: (1) analysis, design, fabrication, and testing of a microchannel heat exchanger with water and liquid nitrogen; and (2) development and

application of a methodology for evaluation of flow-induced vibration of prototype heat exchanger configurations and design to minimize vibration response to coolant flow.

In Part 1 of this study, an analytical model was developed to investigate the fluid and thermal performance of plate-fin-type microchannel heat exchangers for cooling high-heat-load X-ray optical elements. Analyses were carried out to verify that a liquid-nitrogen-cooled microchannel heat exchanger can be designed to maximize heat transfer from silicon to a working fluid. Several assumptions were used to simplify the analytical model. The fully developed laminar flow was modeled by the friction factor expressed as a function of the channel aspect ratio. The thermal performance of the microchannel heat exchanger was modeled by using the developing Nusselt number for laminar flow as a function of the channel aspect ratio and the thermal entrance length. A thermal resistance model was developed as a measure of the thermal performance of a microchannel heat exchanger. A procedure was developed for optimizing the design of a microchannel heat exchanger with the use of the thermal resistance model. A series of calculations were performed through the simplified analytical model to evaluate and compare the flow and heat transfer performance of plate-fin-type microchannel heat exchangers with water and liquid nitrogen. To verify the present analysis, the results of a water-cooled microchannel heat exchanger were compared with the experimental data of Tuckerman and Pease.*

In Part 2 of this study, vibration measurements were performed on two different monochromator silicon crystals, each cooled with liquid gallium. One crystal was circular, with slotted collant channels, and the other was rectangular, with drilled collant channels. The crystals were supported in a laboratory test rig. Vibrations measurements were performed as a function of gallium flow rate, and a procedure - based on selective filtering of the dynamic signal - was devised to extract the vibration response to collant flow.

Technical Progress and Results: Fiscal year 1992 was devoted to (1) development of an analytical model of flow and heat transfer in plate-fin type microchannel heat exchangers and (2) development and application of a methodology for investigating the flow-induced vibration response of liquid-cooled silicon crystal mirrors.

The results of the heat transfer analysis demonstrated that the liquid-nitrogen-cooled microchannel heat exchange can dissipate large amounts of heat ($\dot{q} \approx 1800$ W/cm^2) with extremely low thermal resistance (R = 0.033°C/W). A comparative study showed that the thermal performance of the liquid-nitrogen-cooled microchannel heat

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*Tuckerman, D.B., and Pease, R.F.W., 1981, "High-Performance Heat Sinking for VLSI," IEEE Electron Dev. Lett. EDL-2, p. 126.

exchanger is enhanced as much as three times over that of flowing water through microchannels; see Fig. 1. The results also showed that the coolant flow in the microchannels is laminar. As a consequence, flow-induced vibration can be expected to be minimized in a microchannel heat exchanger.

In the second part of the study, which focused on flow-induced vibration, analysis of the data from vibration tests on two different silicon crystal mirrors showed that the increase in vibration response with flow rate followed a power law with an exponent of approximately 2 for the case of the circular crystal with slotted flow channels, and in the range of 1.5 to 1.8 for the rectangular crystal with drilled flow channels; an exponent of approximately 2 is indicative of turbulence excitation. Figure 2 provides a representative result showing the flow-induced vibration response of the circular mirror as a function of gallium flow rate. Here, it should be noted that the measurement includes turbulent momentum transfer in the headers. These were the first measurements of flow-induced vibration of a monochromator and served to establish a methodology for evaluating various heat exchanger configurations, including headers and flow channels, from the standpoint of flow-induced vibration. Plans were formulated for studying the vibration of a rectangular crystal design measuring 3 x 10 in. and containing 2-mm-diameter drilled coolant holes. The plans call for simulating the crystal with an aluminum plate and using water as the fluid.

The most original and distinctive feature of our findings in this project is that the microchannel heat exchangers can *minimize both thermal resistance and flow-induced vibration.* This makes them ideally suited for the APS applications in which both high heat dissipation and abatement of flow-induced vibration are critically important for beam quality. It is believed that the findings resulting from the thermal analysis will eventually be confirmed experimentally, when prototypes of microchannel heat exchangers are developed specifically for the APS applications. A future goal is to demonstrate that with the microchannel heat exchangers, the high-heat-load X-ray optical elements can be successfully cooled with minimal flow-induced vibration. This will require consideration of the effects of header and inlet/outlet piping design on flow-induced vibration, as well as the effect of the flow in the microchannels, because the former may be controlling.

Specific Accomplishments:

Publications include:

"High-Performance Microchannel Heat Exchanger for Cooling High Heat Load X-ray Optical Elements," U. S. Choi, C. S. Rogers, and D. M. Mills, presented at the Session on Advanced Micromechanical Systems at the ASME Winter Annual Meeting, November 8-13, 1992, Anaheim, CA.

"Vibration Response of a Circular Gallium-Cooled Crystal Mirror with Slotted Flow Channels," J. A. Jendrzejczyk, M. W. Wambsganss, and R. K. Smith, ANL/MCT/TMS-2, July 1992.

"Vibration Response of a Rectangular Gallium-Cooled Crystal Mirror with Drilled Flow Channels," J. A. Jendrzejczyk, M. W. Wambsganss, and R. K. Smith, ANL/MCT/TMS-3, August 1992.

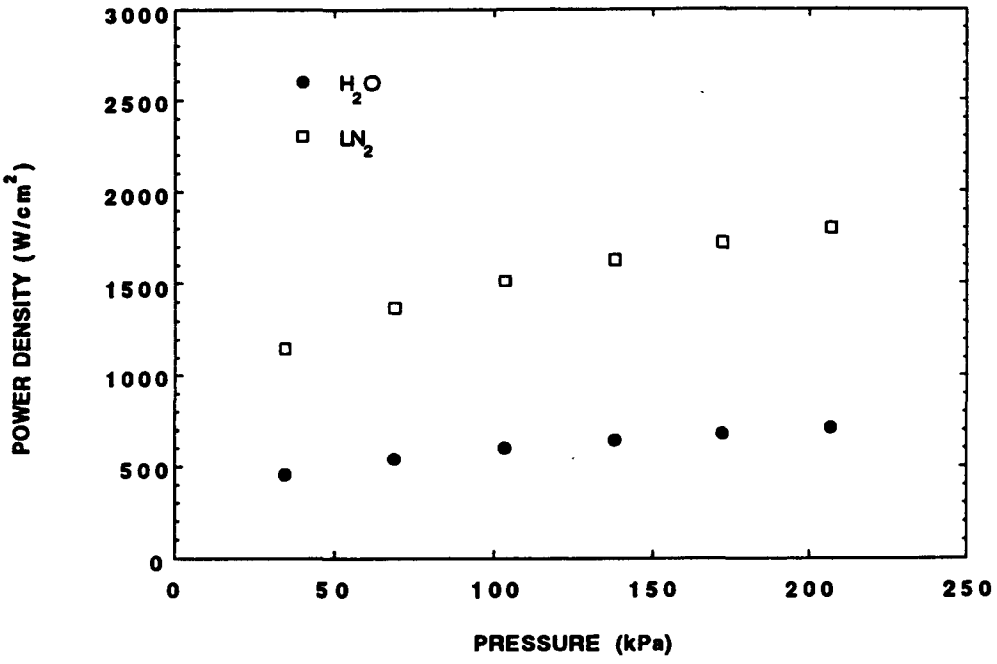

Fig. 1. Power density as a function of pressure drop for water- and liquid-nitrogen-cooled microchannels

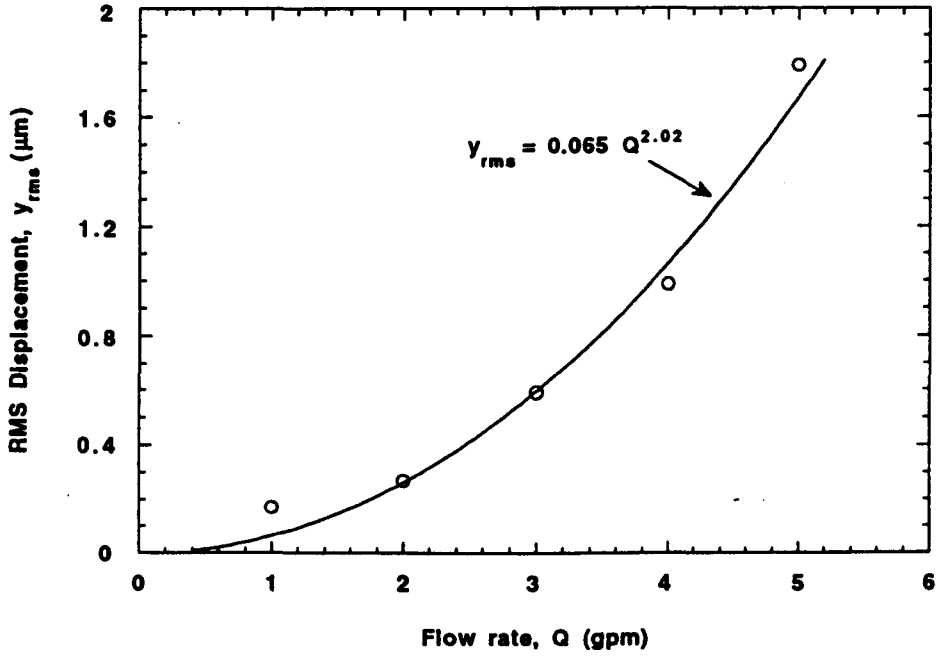

Fig. 2. RMS displacement (y_{rms}) of the circular crystal mirror as a function of gallium flow rate (Q); o measured response, —— curve fit

90-007R2 -- ANALYSIS AND EVALUATION OF ANL MAGLEV CONCEPTS

Associate Laboratory Director Area: Energy, Environment, and Biological Research

Principal Investigators: D. Rote and H. Coffey, Energy Systems
J. Hull and T. Mulcahy, Materials and Components Technology

Funding History:

FY 1990	$169.5K
FY 1991	$256.1K
FY 1992	$106.6K
FY 1993	$ 0K
FY 1994	$ 0K

Purpose: To analyze and evaluate the merits of several concepts for magnetically suspending, guiding, and propelling passenger and freight vehicles that have been invented at ANL. To select the most promising of these concepts or combinations thereof for possible future development and commercialization. To illustrate the value of research and development conducted in a national laboratory environment and set the stage for a major R&D maglev research program.

Approach: Beginning with the establishment of the Argonne Experimental Initiative on Maglev (AXIOM) program in February of 1990, experimental and analytical capabilities were developed to gain an expertise in the evaluation of Maglev technology. The experimental facilities were used to verify new and revised computer codes and investigate and explore outstanding issues that were not capable of analytical investigation. The verified computer codes were used to evaluate and extend old and new Maglev technologies that originated both outside of and at ANL.

In the course of developing state-of-the-art capabilities, eight important new ideas relevant to Maglev technology were developed and six were reported in invention disclosures. Recently DOE has applied for patents on five of these and a sixth is in progress. Also, several proposals were made in the open literature to modify existing technology for application to Maglev systems. However, none were subjected to peer review.

To verify the technical feasibility and evaluate claimed benefits of these innovative concepts and proposed transfers of technology, a panel of active ANL researchers in Maglev technology was assembled: H. Coffey (ES), S. Chen (MCT), J. He (ES), J. Hull (MCT). T. Mulcahy (MCT), and D. Rote (ES). Additional mandates to the panel were: to evaluate the utility of each concept relative to the existing technology, to

identify any additional effort necessary to increase confidence in a concept, and to set priorities for additional development and commercialization, if warranted.

Technical Progress and Results: Fiscal years 1990 and 1991 saw the installation and modification of Cornell's large rotating wheel and the construction of a small rotating drum for use in the verification of computer codes (Levitate, PE2D, and Elektra) developed to predict the steady-state levitation, drag, and guidance forces and magnetic fields associated with continuous guideways. Also, a small turntable, to evaluate the transients created by joints in continuous guideways, and a small rotating wheel apparatus, to investigate the Alternating Gradient levitation concept, were designed and built. Further, a small plastic drum test apparatus was created to provide data for the verification of a computer code "COILGDWY" developed at ANL that uses dynamic circuit theory to predict the levitation forces associated with guideways composed of arrays of discrete coils. The experiments were finished in January 1992 while analysis and predictions using the verified codes are finding continued use in the evaluation of the System Concept Designs (SCDs).

During fiscal year 1992, detailed computations and analyses of several of the ANL-invented concepts was carried out and one or more proponents of each new invention or proposal made a presentation to the panel, followed by discussions and analysis. The following conclusions and recommendations were reached:

1. Expansion Joint for Maglev Guideway (AN-IN-91-12), by T.D. Rossing.

   Experimental proof of concept studies were complete and no further work is required. The invention has merit and has been made available to the one SCD contractor that has a continuous guideway that must be designed to avoid thermal buckling.

2. Propulsion and Stabilization System for Magnetically Levitated Vehicles (AN-IN-90-56), by H.T. Coffey.

   DOE has applied for a patent on the concept. During the evaluations, new innovations were conceived by the panel and a new invention is in the process of disclosure. Both the original and new invention would be strengthened if supported by quantitative evidence that both DC and AC magnetic fields are reduced in the passenger compartment, due to the innovative positioning of the superconducting magnet and linear synchronous motor (LSM) coils.

3. Magnetic Levitation Configuration Incorporating Levitation, Guidance, and Linear Synchronous Motor (AN-IN-90-57), by H. Coffey.

DOE has applied for a patent on the concept. The large number of innovations added during fiscal year 92 strengthens the original invention. The new embodiments need to be clarified and condensed into an addendum and quantitative performance information added to make the disclosure more viable.

4. Attractive Levitation Using Superconducting Magnets with Large Clearance and Alternating Gradient Stabilization (IEEE Trans. Magn. 25, 3272-3274 (1989), by J. Hull.

   The concept is interesting and has proven useful in accelerator technologies, but experimental verification is required to prove its viability in transportation systems. A "proof of concept" bench-scale experiment was designed and conducted and found to be unsuccessful. Since verification can't be performed at a small scale and the concept is in the public domain, there is little incentive for its further development by ANL.

5. Maglev System Concept Using 20-K HTSCs and Hyperconductors (Proc. Intersociety Energy Conversion Engineering Conf. 4, 570-575 (1991) by J. Hull and J. He. Presented in Boston, Ma, Aug 4-9, 1991.

   A Maglev system with a passive guideway and an on-board linear induction motor (LIM) appears possible, if liquid-hydrogen (LH) fueled turbines can be adapted to a Maglev vehicle set consisting of two or more cars in a cost effective and safe manner. Also, additional development of the concept is timely for an early use of a nonpolluting fuel and High Temperature Superconducting (HTSC) powder-in-tube Barrium Strontium Copper Oxide (BSCO) superconducting magnets cooled with LH. Further analysis was judged to be warranted and is in progress.

6. Parallelogram-Shaped Coil Arrays for High-Speed Electrodynamic Maglev Suspension, Guidance, And Directional Switching (ANL-IN-91-103) by J. He and D. Rote.

   This appears to be a viable and potentially more economical alternative to Japan's null-flux system that sacrifices lift/drag ratio (1/3) for simpler guideway construction, electronic switching, and better guidance. Innovations were suggested for increasing the lift/drag ratio and more parameter studies were recommended. The invention should be re-evaluated when the government-sponsored null-flux System Concept Definition costs are reported. Subsequently, further computations and analysis resulted in an addendum to the original invention disclosure. A private firm has developed an innovative propulsion system (proprietary) and is seeking a compatible levitation and guidance system. The levitation and guidance system described here may be just what is needed - however, further analysis is required. In addition to the analysis and panel

deliberations reported above, detailed computations and analysis on two other invention disclosures were conducted in FY92 but there was insufficient time to convene panel meetings to review them. Panel meetings are planned for October. These efforts are summarized below:

7. *Integrated Null-Flux Suspension System for Magnetically-Levitated Vehicles* (ANL-IN-91-13) by D.M. Rote, J. He, and L. Johnson.

   A theoretical model of this concept was developed and a computation code was prepared and used to demonstrate the technical feasibility and viability of the concept. An oral presentation describing the theory and numerical results was given at a Maglev Session of the World Conference on Transportation Research (WCTR) in Lyon, France in June. DOE has applied for a patent on this idea.

8. *Improved High Speed Maglev Design* (ANL-IN-91-67) by D.M. Rote, J. He, and H. Coffey

   A theoretical model of this concept, which incorporates a double-sided linear synchronous motor (DSLSM) and a keel-like structure below the vehicle containing strong-field superconducting magnets, was developed and detailed computations were carried out of forces and magnetic field distributions. The concept was found to be technically feasible and viable and the DSLSM design very efficient compared with existing alternative designs. Several minor modifications to the original invention disclosure resulted from the analysis. Since this invention focuses on the propulsion system, additional work on the design of a compatible levitation and guidance system was judged to be highly desirable. Two concepts are being considered, one is the subject of ANL-IN-91-103. DOE has applied for a patent on this idea.

Specific Accomplishments:

PATENTS: DOE has applied for 5 patents covering ideas developed during the LDRD-sponsored AXIOM program. A sixth invention is being considered for a patent application as well.

NEW INVENTION DISCLOSURES:

1. Double Row Loop-Coil Configuration for High-Speed Electrodynamic Maglev Suspension, Guidance, and Directional Switching - Oct. 8, 1992 - J. He and D.M. Rote.

   - a revision of ANL-IN-91-103

2. A Null-Flux Configuration Incorporating Opposing LSM Coils - a new invention, disclosure in preparation by H. Coffey, J. He, J. Hull, T. Mulcahy, and D. Rote, Aug. 21, 1992.

   - invented during panel evaluation of ANL-IN-90-56 by H. T. Coffey

CONFERENCE PAPERS:

3. Computer Model Simulation of Null-Flux Magnetic Suspension and Guidance, by J. He and D.M. Rote, presented at the WCTR in Lyon, France, June, 1992.

4. Combined Suspension and Propulsion System for Maglev Vehicles, by D.M. Rote, J. He and L.R. Johnson, presented at the WCTR in Lyon, France, June, 1992.

JOURNAL ARTICLES:

5. Edge Effects on Forces and Magnetic Fields Produced by a Conductor Moving Past a Magnet, by T.M. Mulcahy, J.R. Hull, and J.D. Almer, IEEE Trans on Mag. 28, No 5, Sept. 1992.

6. Investigation of the Stability of AC Repulsive-Force Levitation Systems for Low-Speed Maglev, by J. He, Z. Wang, D.M. Rote, and S. Winkelman, IEEE Trans. on Mag. 28, Nov 5, Sept. 1992.

DATA BASES: Several data bases have been established from experiments conducted during the AXIOM program. These have been used to validate computer codes that have, in turn, been used to evaluate the ANL inventions and concepts defined in Federal government-sponsor System Concept Definition Contracts.

FY 1992 LDRD Annual Report (Appendix A)

New Starts in the FY 1993 LDRD Program

This appendix presents brief statements of scope for each new FY 1993 project approved to date. Current authorized and projected future funding amounts for each project are included. Continuation of a project and future funding level are highly dependent on current progress and evolving laboratory priorities. Thus, figures for future years are estimates at best.

About 9% of the anticipated FY 1993 total program cost is being held for commitment later in the year. To date, $9.0M has been allocated to 31 new projects plus 21 projects continuing from a prior year. The expenditure cap approved for Argonne by DOE for FY 1993 is $12 million or about 3% of the projected FY 1993 Laboratory operating budget.

1993 LDRD PROJECT SUMMARY

Proposal Number	Authorized Funding	Principal Investigator(s)	TITLE
93-002N	1993 / $240K 1994 / $300K 1995 / $200	M. Bedzyk M. Ramanathan P. Montano	**Design of New Devices for Production of Elliptically Polarized X-rays** Initiate design and test prototypes of new optical components for an elliptical multipole wiggler beam line at APS. Design the elliptical motion multipole wiggler device with the desired characteristics for the scientific program of the Physical Research beam line at APS. Perform preliminary tests of the optical components at NSLS.
93-003N	1993 / $210K 1994 / $250K 1995 / $150K	G. Knapp P. Thiyagarajan M. Ramanathan	**Development of Small Angle Scattering and Anomalous Small Angle Scattering Techniques** Develop new optics schemes and high speed area detectors to enable the design of the Small Angle X-Ray Scattering station on a beamline at APS.
93-004N	1993 / $320K 1994 / $450K 1995 / $400K	P. Cowan H. Berry D. Gemmell Y. Azuma	**Atomic, Molecular and Optical Physics with X-Rays** Development of equipment needed to study deep inner-shell double-photo-excitation, photoionization of open-shell atoms, resonant and near threshold excitation and decay processes, and x-ray optical physics. In particular, new x-ray interference optics for hard x-rays, a new design for a high temperature atomic oven to provide high density vapor targets, and a novel angle-resolved electron spectrometer will be developed.
93-006N	1993 / $120K 1994 / $200K 1995 / $100K	J. Norris L. Chen M. Bowman D. Tiede J. Tang M. Thurnauer	**Excited State Atomic Structure Determination Using Synchrotron Radiation** Prove the feasibility of performing the first time-resolved EXAFS structure study of photoinduced electron transfer reactions at NSLS.

93-007N	1993 / $ 60K 1994 / $170K 1995 / $180K	S. Riley	**Development and Characterization of Transition Metal Cluster Beams for X-Ray Absorption Studies** The use of a high repetition-rate copper vapor laser for vaporization of refractory metals will be explored. Issues of laser focussing and target and source cooling will be investigated. Diagnostic techniques will be developed to characterize the density, stability, temporal profile, and size distribution of the resulting cluster beams. Such beams will be needed for future x-ray absorption studies.
93-008N	1993 / $ 79K 1994 / $ 90K 1995 / $ 90K	D. Levine M. Henderson R. Stevens	**Parallel I/O** Study common I/O access patterns in scientific applications by tracing existing and nascent Grand Challenge applications of interest to Argonne's high-performance computing program and develop synthetic benchmarks. Design and implement efficient algorithms for system resource management based on this information. Develop and investigate techniques for choosing data partitioning, placement, and migration policies. Develop algorithms and software to gather application I/O access patterns automatically. These efforts should lead to high-performance, parallel I/O systems software that supports massively parallel applications.
93-009N	1993 / $200K 1994 / -0- 1995 / -0-	R. Pardo J. Nolen	**Development of Rare-Material Capability for Ion Beams at ATLAS** Develop new techniques for the production of beams of very low-abundance nuclear species, both stable and, to a lesser extent, radioactive. This goal will be achieved by improving by a large factor the ionization efficiency of the electron cyclotron resonance ion source at ATLAS. This advance in source technology will make it possible for the research program at ATLAS to be effective in several new areas.
93-010N	1993 / $160K 1994 / $200K 1995 / -0-	D. Werst A. Trifunac J. Proudfoot D. Underwood	**Radiation-Hard Scintillator Materials Via Organic Modification of Amorphous Silica** Sol-gel methods will be used to make silica castings or coatings impregnated with organic dyes. These composite materials will be tested for transparency, dye photostability and scintillation efficiency and light output. Radiation damage to the dye will be determined optically. Formation of lattice defects in the glass will be determined optically and by EPR to reveal the chemical/structural nature of any radiation damage.

93-038N	1993 / $200K 1994 / $200K 1995 / $200K	D. Pedersen D. Hill	**Application of World Wide Lessons Learned to Advanced IFR Plant Design and Operation.** Evaluation of the technical successes and problems at reactors in other countries and determination of the technical implications of these on advanced IFR designs.
93-039N	1993 / $250K 1994 / -0- 1995 / -0-	L. Monson H. Planchon	**Inservice Inspection and Monitoring of Sodium Mechanical Systems** Develop techniques for acoustically monitoring the status, beyond mere position, of equipment (both active and passive) in sodium systems utilizing three dimensional, real-time computer imaging capabilities. Such parameters as structural integrity, embrittlement status, dimensional changes, leak detection, weld inspection, loose parts, etc., may be accessible from acoustic data.
93-040N	1993 / $220 1994 / $120K 1995 / $120K	K. Carney S. Frank S. Johnson	**Laser Based Hot Cell Elemental and Isotopic Analysis System** Introduce laser based analytical methods for direct elemental quantification at trace, minor and major levels in a hot cell environment. Reduce the need for complex labor intensive sample dissolution techniques, while providing accurate, rapid analyses of irradiated fuel, salt, cadmium and various waste samples. Demonstrate techniques that could be adapted directly to the production floor of a fuel cycle facility.
93-041N	1993 / $150K 1994 / $100K 1995 / $100K	L. Leibowitz M. Petri S. Tam J. Richardson M. Mueller	**Development of Synchrotron Radiation Analytical Capabilities for the Study of Nuclear Materials** Development of innovative synchrotron radiation analytical techniques for nuclear materials will be conducted using the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) with the view of progressing to Argonne's Advanced Photon Source (APS). The project will involve developing high-resolution collimated-beam micro-diffraction. Furthermore, an advanced sample holder design suitable for plutonium-bearing samples will be tested. X-ray focusing techniques for micro-diffraction, micro-fluorescence, and extended X-ray absorption fine structure (EXAFS) analyses will be optimized. These techniques are uniquely suited for studying key fuel-cladding compatibility and IFR materials issues.

93-042N	1993 / $250K 1994 / $250K 1995 / -0-	D. Spence	**Development of a CW Ion Injector for High-Current Accelerator Applications** Develop a generic high-brightness hydrogen ion injector suitable for use in a high-current, continuous wave (cw), superconducting (SC) accelerator system. An electron cyclotron resonance ion source coupled to an appropriate extractor design will be tested.
93-043N	1993 / $250K 1994 / $250K 1995 / -0-	J. Braun H. Planchon	**Implement Reliability Centered Maintenance and Condition Monitoring at EBR-II** Expand the practices used in the maintenance activities at EBR-II to become as sophisticated as the best practices in the civilian industry today and then advance the state of the art by introducing innovative data collection, coordination and computer technology.
93-044N	1993 / $ 90K 1994 / $150K 1995 / $ 80K	R. Singer D. Hill R. Seidensticker	**Implications of Design and Safety Criteria for Fuel Transfer in an Advanced IFR Reactor/Fuel Cycle Facility Interface** Identify and evaluate the key safety criteria that govern the fuel transfer process between the nuclear island and the fuel cycle facility in an advanced IFR and, from these criteria, set design requirements for in-vessel storage, fuel transfer machinery and fuel cycle process equipment together with cooling time and heat load limits for spent subassemblies.
93-045N	1993 / $200K 1994 / $230K 1995 / -0-	J. Delayen	**Transport of a High-Current Beam through a Superconducting Structure** Perform the first transport experiment of a high-current ion beam through a superconducting radio-frequency quadrupole (RFQ) structure, and demonstrate the applications of superconducting accelerator technology for high-currents. Technical focus will be to evaluate the amount of beam impingement and gas condensation that can be tolerated by a superconducting structure in an accelerator.

93-046N	1993 / $300K 1994 / $275K 1995 / $175K	R. Clarksean	**Development of Advanced Control Interfaces for Robotic Applications in Remote Systems** Interface remotely-operated telerobotic manipulators with computer graphics workstations for improved control and capabilities. The automation of manipulators will allow for an increase in precision, repetitive operation, productivity, and allow for safer operation. Current robotics modeling software considers path planning, obstacle avoidance, and task. This project would interface an available computer-graphics workstation with an available robotics manipulator to demonstrate the capabilities of such an integrated system.
93-047N	1993 / $210K 1994 / $210K 1995 / $175K	K. Gross	**Online IFR Fuel Burnup Determination via Stable-Gas Mass Spectrometry** Develop a low cost, fast response, accurate method to measure burnup of IFR fuel pins upon completion of irradiation and prior to reprocessing, with an analysis turnaround time suitable to support mass flow rates for a commercial IFR. Explore the feasibility, practicability, and attainable accuracy for a gas-sniffer system connected to an online mass spectrometer in the Fuel Cycle Facility. The mass spectrometer will quantify, to precision better than 1%, one or more ratios of stable noble-gas isotopes whose compositions vary monotonically with fuel burnup. This new capability, if proven successful, may provide an alternative to the lower accuracy, time-consuming and costly wet chemistry techniques for fuel burnup determination.
93-088N	1993 / $ 65K 1994 / $400K 1995 / -0-	M. Petrick A. Wolsky	**Feasibility Study of the Conversion of the Large Bore 6 T Magnet to an MRI User Facility** Collect the information and data needed to decide the merits of converting ANL's 6 T large bore, saddle coil magnet to an MRI Facility. At such a facility, the researcher can use the facility's set of rf, gradient and pick-up coils designed to be applicable in many areas, or provide and install his/her own set of coils.

93-089N	1993 / $295K 1994 / $ 60K 1995 / -0-	R. Reck	**Exploratory Investigation of Macroscopic Planetary Atmospheric Physical and Chemical Processes Utilizing Modeling and Remote Sensing Techniques** Perform exploratory studies of different scales of planetary physical and chemical processes using laboratory measurements, modeling and remote sensing methods. Three principal areas of research will be considered; modeling of regional climate processes, photochemistry of the atmosphere, and remote sensing and smart systems (neural network) studies of climate and terrestrial ecosystems.
93-090N	1993 / $285 1994 / $187K 1995 / $198	R. Stevens E. Huberman	**Development of Computational Biology Methods** Develop methods for computational structural biology in four areas: (1) Protein Folding/Design; (2) Drug Design; (3) Enzyme Design Catalysis; and (4) Structural Determination and Analysis. In each area the project will develop parallel molecular models and fast X-ray crystallography systems.
93-091N	1993 / $ 95K 1994 / $100K 1995 / -0-	S. Pratt J. Dehmer P. Dehmer E. McCormack	**Laser-Induced Transient Gratings** Develop a class of nonlinear optical detection techniques for remote gas-phase chemical analysis and the study of chemical dynamics. Exploratory work on laser-induced transient gratings and degenerate four-wave mixing will be performed to determine their suitability for excited-state absorption spectra and their applicability to remote detection and chemical analysis. Laser-induced-grating techniques will record the excited-state absorption spectrum of a stable molecule. This will address the sensitivity of the technique and assess the difficulties in determining optical properties from the laser-induced-grating and degenerate four-wave mixing and real-time holography. These methods will be tested on short-lived molecular species to evaluate suitability for studying transient species.
93-092N	1993 / $195 1994 / $250 1995 /	G. Dyrkacz P. Bonsignore	**Chemical Feedstocks for High Performance Polymers From Coal** Investigate efficient methods for the production of chemical intermediates from coal that can be used to produce novel, high value polymers. The work will be conducted in two phases; (1) the generation and isolation of aromatic chemical intermediates from coal, and (2) the synthesis and study of the properties of plastics derived from these intermediates.

93-093N	1993 / $122K 1994 / $267 1995 / $285	E. Huberman J. Hoheisel	**Integral Mapping Analysis of the Human Chromosome 3** Physical mapping of one of the largest human chromosomes, chromosome 3, will be performed using cloning systems that can accommodate the largest inserts of human genomic DNA.
93-094N	1993 / $ 90K 1994 / $ 90K 1995 / -0-	R. Sekar	**NO_x Reduction in Diesel Engine Exhaust Using a Nitrogen Plasma** Two devices, one using an arc discharge and the other using a corona discharge, which produce nitrogen plasma will be built and tested. The preferred method of electrically activating nitrogen will be determined. Reductions in NO_x will be determined from engine tests.
93-095N	1993 / $ 57.5K 1994 / -0- 1995 / -0-	R. Kumar P. Nelson M. Krumpelt	**Low Temperature Solid Oxide Fuel Cells for Transportation Applications** Data on the chemical and mechanical behavior of metal alloys suitable for solid oxide fuel cell application will be reviewed. Candidate metal alloys for fabrication of metallic components will be tested. A design and modeling study will be conducted to establish the requirements of all cell components. Complete fuel cell stacks will also be modeled to determine appropriate cell and stack dimensions and to demonstrate the promise of the performance of the new design for transportation applications.
93-096N	1993 / $120K 1994 / -0- 1995 / -0-	D. Weber R. Valentin R. Kulak A. Tenter C. Mueller E. Plaskacz T. Canfield	**Advanced Automotive Engineering Through High Performance Computing** To develop next generation computational structural mechanics and fluid dynamics for automotive engineering applications based on massively parallel computer architectures. Related to computational structural mechanics, with anticipated applications in crash-worthiness, metal forming and linear dynamics applications, are two tasks: (1) developments of parallel h,p-method techniques for linear finite element analysis and (2) development of parallel non-linear structural analysis. Related to computational fluid dynamics, with anticipated applications to combustion systems analysis and underhood air flow and engine heat transfer problems, are two additional tasks: (1) a 3--dimensional multiphase, multi-component compressible hydrodynamic model and (2) a 3-dimensional CFD code for thermally driven flows.

	1994 / $ 20K 1995 / $ 20K		**with Site Directed Mutagenesis** Grow single crystals for x-ray diffraction and characterization of electron transfer reactions of genetically modified reaction center proteins. This will lead to experimental determination of the detailed mechanistic role of "solvent" in electron-transfer chemistry.
93-150N	1993 / $181K 1994 / $200K 1995 / $100K	I. McNulty B. Lai W. Yun E. Gluskin	**Novel Applications of Undulator Radiation: Holography, Intensity Interferometry and Speckle** Study the feasibility, develop the needed optics and instrumentation, and experimentally demonstrate the underlying principles of three x-ray methodologies making use of 0.1 to 1.0 nm wavelength, high-brilliance undulator radiation: Techniques to be developed are holography, intensity interferometry, and speckle.
93-151N	1993 / $186K 1994 / 200K 1995 / $200K	R. Kustom	**Millimeter Wave Linac and Undulator Development Using Microfabrication Techniques** Candidate millimeter wave RF structures for the linac and for a microfabricated mm-wave undulator will be developed and a target parameter regime will be established. Ten-times scale models will be built and their RF characteristics tested in the laboratory. Manufacturing techniques for building the mm-wave-sized components (such as electron gun, cavities, quadrupole magnets, etc.) will be developed.
93-152N	1993 / $181K 1994 / $150K 1995 / $250K	W. Yun E. Gluskin	**Development of Interferometer-based Fourier Transform X-Ray Techniques** Develop interferometer-based Fourier transform x-ray techniques and explore their applications to spectroscopy and imaging of surfaces and interfaces. These techniques will offer many unique capabilities originating from the use of interference of a signal beam of interest with a reference beam and the use of Fourier transformation of the x-ray signal through optical means.